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the potential sensitivity of drinking water supplies to acidic precipitation in canada

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THE POTENTIAL SENSITIVITY OF DRINKING WATER SUPPLIES TO ACIDIC PRECIPITATION IN CANADA

Environmental Health Directorate
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1. INTRODUCTION

Since the late 1960s, there has been increasing international interest in the long-range transport of air pollutants. Specific effects of sulphur and nitrogen oxides, which are precursors of acidic compounds that cause acidic precipitation, were noted in Scandinavian lakes in 1972. Further investigation confirmed that there were ecosystem effects related to sulphur and nitrogen oxides from distant source regions (OECD 1977). Indeed, prolonged transport enables the chemical transformation from sulphur and nitrogen oxides to acidic compounds.

Oxides of sulphur and nitrogen are emitted from a wide variety of sources which are widely distributed geographically (e.g., from combustion of fossil fuels). Also, a large part of Canada is geologically similar to Scandinavia where ecosystem damage has occurred. Consequently there has been growing national concern about the problem. There are several specific regional features suggesting the need for further study:

1. Emissions of sulphur dioxide (SO_2) in the United States and Canada are estimated to be 25.7×10^6 tonnes and 5×10^6 tonnes, respectively. Emissions of nitrogen oxides (NO_x) in the two countries are estimated to be 22.2×10^6 tonnes and 1.9×10^6 tonnes, respectively (U.S. - Canada Research Consultation Group 1980). Although only modest increases are expected in future SO_2 emissions, larger NO_x emissions are anticipated from increased use of fossil fuels. Large fractions of the emission sources are in the northeastern and mid-west United States (e.g., Ohio Valley).

2. Meteorological conditions in eastern North America are conducive to pollutant transport from major source regions in the United States to southern Ontario, Quebec, and the Maritime Provinces. Models of transboundary flux predict U.S. to Canada sulphur deposition to be 1.3 times in winter and 3.2 times in summer that of Canada to the U.S. (U.S. - Canada Research Consultation Group 1980).

3. Wet and dry sulphate depositions in eastern Canada are occurring at rates similar to those experienced in Scandinavia.

4. A large part of eastern Canada is underlain by resistant granitic and siliceous bedrock, from which calcareous deposits have been removed by glaciation. Although variable, soils are generally non-calcareous and often acidic podzolic or organic soils. These bedrock and soil types are most susceptible to acidic precipitation.

Annual average precipitation pH in eastern North America has decreased in the last two decades, with areas experiencing precipitation pH$<$4.6 expanding considerably (Likens et al. 1979). The influences of acidic precipitation, including decreased pH and alkalinity and increased sulphate, have been observed over a twenty-year period in river basins of southern Nova Scotia, remote from anthropogenic sources (U.S. - Canada Research Consultation Group 1980).

The gradual accumulation of acidic compounds and other airborne materials over long periods of continuous deposition creates cumulative ecosystem effects. One potential effect of interest is the increased mobilization and biological availability of trace elements. The solubilities of aluminum and iron have long been known to increase with increasing acidity (Dobrsanski and Wondrausch 1963). Other trace elements may be similarly affected. It has recently been suggested that with increasing acidity, lead and mercury are released from sediments as bacterially transformed methylated species, whereas arsenic and selenium are not so affected (Mayfield 1980).

A potential cumulative effect of acidic precipitation is the acidification of drinking water supplies. The primary health implications of this effect arise from the mobilization of trace elements from geological or anthropogenic sources in the watershed, or from materials in the water distribution system. Acidification of water supplies has been shown to cause toxic levels of copper in tap water standing overnight in the Adirondack region of New York (Legislature of the Province of Ontario 1979).

The potentially deleterious health effects of asbestos have recently received considerable attention. Water distribution systems using appreciable quantities of asbestos - cement piping are susceptible to mobilization by asbestos following dissolution of the calcareous component by acidic water.

It is not known with certainty whether continuing acidic precipitation in Canada will cause a health hazard in municipal drinking water supplies, nor is it known which water supplies are most susceptible to the effects of acidification.

The Ontario Ministry of the Environment has recognized the potential water quality problems that may arise in poorly buffered municipal water supplies. Acidic conditions may occur not only from acidic precipitation, but also from chemical treatment of poorly buffered water prior to distribution. Municipal water treatment now includes the addition of soda ash ($Na_2(CO)_3$) for alkalinity adjustment or lime ($Ca(OH)_2$) for pH control in several Ontario water supplies on the Canadian Shield.

The objective of this report is to describe and illustrate the fundamental factors contributing to a water supply's susceptibility to acid precipitation effects. Specific examples are used from several regions in Canada. Because variations in bedrock and overburden conditions may have significant localized effects, the examples will not necessarily be indicative of conditions in all drinking water supplies in that region. Each water supply should be assessed on an individual basis.

This report will also present a methodology by which individual assessments can be done. The methodology will be based upon indicators of a watershed's potential sensitivity to acid precipitation, including bedrock and overburden type, watershed characteristics, water chemistry, and areal distribution and pH of precipitation. Assessments of individual water supplies by this method will demonstrate their relative susceptibilities to the effects of acidic precipitation.

2. THEORETICAL CONSIDERATIONS

The characteristic of acidic precipitation which is of greatest public concern is evident in its name. However, associated with the acidic components are a variety of inorganic and organic materials that may be deposited with rain or dry fallout. Acid precipitation contains a variety of heavy metals. Considerable data from Europe and North America show elevated levels of metals such as Cd, Hg, Pb, Zn, Ag, Au, Cr, Ni, Sb, and V in recent lake sediments. It is postulated that many of these increases are likely because of air pollution from coal combustion. Airborne materials enter surface water supplies both directly by deposition onto the water surface, and indirectly by deposition onto and runoff from the land surface within a watershed. In addition, many elements may be leached out of surficial soils, tills and bedrock and enter surface water supplies.

Acidic precipitation also contains a variety of elements which may be considered beneficial, including Ca, K, S, N, and P, and a variety of organic molecules. Alkanes, polycyclic aromatic hydrocarbons, phthalic acid esters and fatty acid ethylesters, as well as many commonly used industrial chemicals, pesticides, and herbicides are depositied directly onto surface waters, or may enter surface waters after leaching from the terrestrial portion of the watershed (Great Lake Science Advisory Board 1980).

The terrestrial system has a series of complex geochemical and biochemical factors by which the effects of acidic precipitation are mitigated. These factors for a given watershed are dynamic and may be expected to change with time as the buffering or retention capacities become exhausted. Their effectiveness will vary with circumstances such as loading and contact time. For example, during the spring thaw, a winter's accumulation of acidic precipitation and deposition is released into overland flow systems within a very short period of time. The resulting heavy flow infiltrates the soil systems very little because of frozen or saturated grounds. Therefore, even in a region of substantial buffering capacity, a significant pH effect may occur in a water supply during a spring slug acid flow.

At other times of the year, depending upon the specifics of the watershed in question, much of the precipitation may infiltrate the ground and undergo buffering reactions. Acids are neutralized, and metals and organics are retained and prevented from entering surface waters. Any characteristic of a water supply catchment basin which delays input to surface waters and encourages infiltration will reduce the sensitivity of the water supply to acid rain. Such characteristics include 1) a small water surface area to overall catchment basin surface area, 2) a generally flat topography, 3) a high surface infiltration capacity, and 4) a thickness of soil, glacial debris or bedrock through which infiltrating water flows before discharge to surface waters.

Contaminants occurring in surface waters from acidic precipitation undergo a series of chemical and biological interactions which will restrict or enhance their presence in surface water supplies. Many trace elements and organic materials have been shown to complex with organic and inorganic particulates in the water column, and to precipitate as sediments. The rate and degree at which this happens is dependent upon the nature of the particulates and on water chemistry, particularly pH. If a surface water supply has a high production of biological particulates (phytoplankton and zooplankton) and/or a high input of inorganic silt, the potential for contaminant removal to sediments is large. However, low pH circumstances may liberate these same contaminants from their particulate state and return them to the dissolved state.

In general, the longer a contaminant is resident in surface water, the greater will be its potential for removal to sediments. Accordingly, headwaters are more sensitive to the effects of acidic precipitation. Susceptibility to acidification generally decreases with increasing distance downstream in a watershed. In addition, the higher the natural rate of biological productivity in a surface water, the less sensitive the water supply will be to acidification.

Water supplies derived from groundwater reservoirs can generally be considered much less sensitive than surface waters to the effects of acidic precipitation. Certain exceptions, however, may exist in this area where water supplies are obtained from bedrock such as fractured granite where buffering capacities are low, reaction times are short, and contact surface areas are low.

The following section will expand upon the pathways by which acidic precipitation and associated contaminants reach surface water supplies. Reactions occurring within water distribution systems leading to the mobilization of trace metals or asbestos are not covered in this report. The mobilization of trace metals is at present the topic of a study being carried out for the Long Range Transport of Air Pollutants program through Canada Centre for Inland Waters at Burlington, Ontario.

2.1 Atmospheric Acidity

If a raindrop is pure water and at equilibrium with atmospheric gases, its normal pH will be 5.6. This is controlled by carbon dioxide dissolution in the water droplet and subsequent formation of hydrogen ion and bicarbonate ions. If the raindrop is contaminated by gaseous NH_3 and alkaline soil dust (metal carbonates and oxides), the hydrogen ions are taken up, resulting in a higher pH (Liljestrand and Morgan 1981). If the raindrop is contaminated with oxides of sulphur and nitrogen from anthropogenic emissions, a lower pH will result.

Atmospheric acidity is dominated by the presence of low concentrations of two strong acids, sulphuric acid (H_2SO_4) and nitric acid (HNO_3). A strong acid is defined as one which completely dissociates, liberating all hydrogen ions associated with the negative ion. In most inland rainfall samples which are termed acidic, the concentration of hydrogen ion is nearly balanced by the combined concentrations of sulphate and nitrate, on a charge basis. In the Prairies and the Maritimes, rain droplet invasion by other ions such as sodium, calcium or chloride can affect this charge balance somewhat. However, the relative concentrations of sulphate and nitrate usually provide a fingerprint for determining the general source of acidity.

Sulphate concentrations are primarily associated with emissions from power generation plants and mining/smelting operations. Nitrate concentrations are associated with emissions from power generation plants and transportation activities. Oxides of sulphur and nitrogen may be transported for thousands of kilometres from the source, before being removed through dry and wet deposition. The dispersion path taken by the acidic compounds is a function of emission height, particle size (smaller particulates, less than 1 µm, may remain airborne for several days), and geographical and meteorological characteristics.

An estimate of the annual average pH in rainfall is given for North America in Figure 2.1. Using a pH of less than 5.6 as the definition of acidic precipitation, most of eastern Canada is affected to some degree. Parts of the western provinces are also affected, although the effect is generally limited to the west coast. The non-acidic nature of the precipitation of the Prairies relates to the lack of significant acid sources and the effects of alkaline soil dusts. Individual rainfall events may be more acidic than the annual averages shown in Figure 2.1.

Several continental weather systems in eastern Canada, particularly warm frontal precipitation, are associated with air masses that have crossed industrialized urban areas to the south and southwest of the Canada - U.S. border. This results in trans-border migration of acidic precipitation and considerable contribution to regional acidity levels. General air mass movements and principal source strengths in eastern North America are shown in Figure 2.2. It is expected that increased coal development in the U.S. Northern Great Plains will result in some future impact on the Prairies due to the same type of air mass movement.

2.2 Geology and groundwater

Typically, uncontaminated rainwaters of temperate regions are somewhat acidic, their pH values ranging between 4.5 and 6.5 (Carroll 1970). They are neutralized by reaction with consolidated bedrock materials and the solids of surficial deposits such as glacial debris and stream sediments. Rainwaters made more acidic by contaminants are neutralized in a similar manner, except that more materials are needed to neutralize the acidic waters. The capacity to neutralize acids and the rates at which they are neutralized are controlled by: the mineralogy of the bedrock materials, the glacial debris and the weathering products; the permeability of these materials; and the hydrological regime of the considered area. This section will review the types of reactions by which the rainwaters are neutralized, and the influences of mineralogy, permeability and hydrology.

2.2.1 Types of Reactions

Two types of reaction contribute to the neutralization of rainwater. One type is the usual acid-base reaction to produce a salt. An example is the reaction of an acidic solution of H_2SO_4 with a base, calcite ($CaCO_3$):

$$\underset{\text{(acid)}}{H_2SO_4(aq)} + \underset{\text{(base)}}{CaCO_3(c)} \longrightarrow \underset{\text{(salt)}}{CaSO_4} + H_2(aq) + CO_2 \tag{1}$$

The $CaSO_4$ so produced may remain in solution as a dissolved salt, or it may precipitate if the concentration of salt is sufficiently high. The base is consumed by this reaction. Consequently, the effectiveness of the reaction is dependent upon the presence and abundance of the base.

The second type of reaction is similar to an acid-base reaction, except the buffering agents are solids (minerals) in contrast to dissolved constituents. These reactions are of two distinct types: 1) mineral transformation reactions, and 2) cation exchange reactions. It is important to distinguish between the two - the mineral transformation reactions are generally much slower, the cation exchange reactions are typically very rapid. An example of the mineral transformation reaction is the attack of feldspar by an acidic solution to produce a clay mineral (kaolinite):

$$\underset{\text{(acid)}}{H_2SO_4(aq)} + \underset{\text{(feldspar-the-base)}}{2NaAlSi_3O_8 + H_2O} \longrightarrow \underset{\text{(clay mineral)}}{Al_2Si_2O_5(OH)_4} + 4SiO_2(aq) + \underset{\text{(salt)}}{Na_2SO_4(aq)} \tag{2}$$

This is typical of reactions occurring during the weathering of granitic and metamorphic rocks (Garrels 1967). The reaction is complex, but essentially, protons are consumed in the reaction and metal ions are released to solution (Na^+ in the example above) in direct proportion to the amount of acid consumed. All mineral transformation reactions involving aluminous silicates are of this type (Garrels and Mackenzie 1967).

Cation exchange reactions are substantially different in that there is no destruction or formation of minerals. Rather, there is exchange of ions on specific sites in lattices or on their surfaces. The effect of an acid is to displace a metal ion (M^+) at that site and replace the metal by a hydrogen ion:

$$\underset{\text{(Acid)}}{H_2SO_4} + \underset{\text{(Exchanger)}}{2M^+R} \rightleftharpoons \underset{\text{(Exchanger)}}{2H^+R} + \underset{\text{(salt)}}{M_2SO_4(aq)} \qquad (3)$$

Here R represents the lattice on which metal-hydrogen ion exchange occurs. There are no effects on the lattice properties of the exchanger. These types of reactions may proceed on and within any mineral lattice but typically, most exchange takes place on clay mineral lattices (Nesbitt et al. 1980). The metals released to solution during neutralization are determined by the compositions of the minerals being attacked by the acids. The rates at which the reactions proceed are also determined to a great extent by the mineral constitutents. Consequently, the properties of some minerals require discussion.

2.2.2 Common Minerals and Their Properties

The most common minerals of granitic and metamorphic rocks are

quartz (SiO_2),

feldspars ($(K, Na) \left[AlSi_3O_8\right]$),

chlorite ($(Mg,Al,Fe)_{12} \left[(Si,Al)_8O_{20}\right] (OH)_{16}$),

the micas, biotite ($K_2(Mg,Fe^{2+})_{6-4}(Fe^{3+},Al,Ti)_{0-2}$

$\left[Si_{6-5}Al_{2-3}O_{20}\right] (OH,F)_4$), and

muscovite ($K_2Al_4 \left[Si_6Al_2O_{20}\right] (OH,F)_4$).

These minerals are present in sedimentary rocks, but clay minerals such as:

kaolinite ($Al_4 \left[Si_4O_{10}\right] (OH)_8$),
illites ($K_{1-1.5}Al_4 \left[Si_{7-6.5}Al_{1-1.5}O_{20}\right] (OH)_4$), and
montmorillonites ($((1/2Ca,Na)_{0.7}(Al,Mg,Fe)_4 \left[(Si,Al)_8O_{20}\right]$
$(OH)_4.n\ H_2O)$

are also common. Sedimentary rocks include limestones and dolostones, the minerals common to these rocks being calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Bedrock consists of granitic, metamorphic and sedimentary rocks so that all of the above minerals may influence acid neutralization reactions in regions where bedrock materials are the dominant surface solids. Glacial debris is comminuted bedrock material and again all the above minerals may influence acid neutralization reactions in regions where glacial debris deposits are abundant. Weathering profiles generally contain quartz and clay minerals. In areas where weathering profiles are well developed, the clay minerals have the capacity to neutralize acids. Properties of individual minerals are discussed.

2.2.2.1 Quartz

Quartz does not act as a base; consequently, it cannot neutralize acids by reaction (1). Quartz is not transformed to other minerals; therefore, it can not neutralize acids by reactions similar to reaction (2). As well, quartz has an exceedingly small cation exchange capacity (Carroll 1970); and, therefore, it has exceedingly small capacity to neutralize acids by cation exchange as in reaction (3). Summarizing, quartz has virtually no capacity to neutralize acids. Bedrock composed primarily of quartz (quartz-rich sandstones and metamorphic rocks) will not neutralize the acids in rainwater nor will they release metals (including toxic metals) to solution as a result of contact by acidic waters.

2.2.2.2 Feldspars

Feldspars are the largest mineral group in the earth's crust. Feldspar reacts with acids by reactions (2) and (3). The simple acid-base reaction (1) is not applicable because solid products invariably form as it is consumed in reactions. The cation exchange capacity of feldspar is very low and of the same order as that of quartz (Carroll 1970). Consequently, neutralization of acidic rainwaters by reaction with feldspars proceeds via mineral transformation processes (reaction 2), producing clay minerals plus dissolved salts as products of the reaction (Grant 1963; Garrels 1967; Nesbitt et al. 1980). Feldspars are the most abundant of all minerals in granitic and metamorphic rocks and they can be expected to react with acidic rainwaters. Glacial debris may contain abundant feldspar if it is derived from granitic and metamorphic rocks (common in Shield areas), but sedimentary rocks generally contain little feldspar, and mature weathering profiles contain virtually none.

In summary, rocks containing appreciable quantities of feldspars have the capacity to neutralize large quantities of acids if reaction rates are sufficiently rapid. (Reaction rates remain to be discussed.) During neutralization of the acids, no large quantities of metals are produced other than Na^+, K^+ and Ca^{++}, all of which are common and non-toxic constituents of natural waters. Toxic metals will not be released since feldspars do not incorporate these elements in significant quantities (Deer et al. 1967).

2.2.2.3 Micas

The micas include the minerals biotite, muscovite, and for purposes of this discussion, chlorite. As with feldspars, reaction of micas with acids yields solid mineral products and dissolved salts (Garrels and Mackenzie 1967). Consequently, neutralization proceeds only by mineral transformations reactions (reaction 2, with mica acting as the base) and by exchange of cations on and within the mica lattices (reaction 3, with R being the mica lattice). The cation exchange capacities of micas are moderately high (Carroll 1970) and much higher than those of quartz and feldspars. Consequently, cation exchange on micas can be an effective process whereby acids are neutralized. Garrels and Mackenzie (1967) demonstrated that biotite reacts with acids of the weathering environment to produce clay minerals (equivalent to reaction 2), proving that micas can neutralize acids by mineral transformation processes.

Micas are generally present in small amounts in granitic and sedimentary rocks (particularly sandstones). They may constitute reasonable proportions of some metamorphic rocks (muscovite and chlorite being the abundant micas). However, their small proportions in most rocks make them generally unimportant with regard to neutralization of large amounts of acids. Where they constitute an appreciable portion of the bedrock or surficial deposits, they have the capacity to neutralize acids. The micas can incorporate significant quantities of heavy metals into their structures (Deer et al. 1967). If large amounts of mica are consumed in the neutralization reaction, these metals may be released to solution.

2.2.2.4 Clay Minerals

The clay minerals are complex in their chemistry and varied in their properties. Three of the most abundant clay mineral groups are the kaolinite, illite and montmorillonite groups. The three groups, when reacted with acids of the weathering environment, produce solid reaction products such as gibbsite ($Al(OH)_3$) and dissolved salts (Bayliss 1967; Kronberg et al. 1979). As with the feldspars and micas, the clay minerals neutralize acids by mineral transformation reactions (reaction 2, with the clay minerals acting as the base and gibbsite the solid product) and by cation exchange (reaction 3, with the clay minerals representing R). The cation exchange capacities of the clay mineral groups vary, with the montmorillonite group displaying the highest, and the kaolinite group the lowest capacities (Carroll 1970). The montmorillonites, with their large cation exchange capacity, are capable of neutralizing large quantities of acids by cation exchange alone. They also have the capability of neutralizing acids by mineral transformation reactions (analogous to reaction 2). Of the clay minerals and all minerals thus far discussed, montmorillonite has the greatest capacity to neutralize acids. Illites have somewhat lower cation exchange capacity but the neutralization capacity of illite is still greater than that of most minerals. Illites can also neutralize acids by mineral transformation reactions. Kaolinite has a moderately low exchange capacity and its capability to neutralize acids by exchange is limited. Kaolinite cannot neutralize acids by mineral transformation reactions as it contains no cations which can be readily released to solution to replace consumed H^+ ions (reaction 2). Aluminum is unavailable because it forms the insoluble hydroxide, gibbsite ($Al(OH)_3$) as a reaction product (Kronberg et al. 1979). While montmorillonite has a great capacity for neutralizing acidic rainwaters, illite has a somewhat lower capacity and kaolinite has a very low capacity, probably lower than that of feldspar and approaching that of quartz.

Granitic and metamorphic bedrocks contain little or no clay minerals. Of the sedimentary rocks, quartzose sandstones contain only small quantities of clay minerals; dirty sandstones such as graywackes contain appreciable quantities; and shales may contain up to 70 to 80 per cent clay minerals (Pettijohn 1975). Glacial debris may or may not contain significant quantities of clay minerals, depending upon the original materials contributing to the glacial products. Weathering profiles contain abundant clay minerals, the kaolinites being concentrated in the most weathered portion of the profile and illites and montmorillonites being concentrated in the lower, less weathered parts of the profile. In general, surficial deposits (glacial debris, stream sediments and weathering profiles) often contain appreciable quantities of clay minerals. If these clays are predominantly illites and montmorillonites, they are capable of neutralizing large quantities of acids. However, if kaolinite is the dominant clay mineral, their neutralization capacity is low.

Clay minerals with high cation exchange capacity accept transition metals such as copper and zinc onto their exchange sites (Hall 1980). If these metals are present, they may be released to solution during acid neutralization, resulting from displacement by H^+. However, large quantities would be released only if the clay minerals were 'contaminated' by some unusual means, because these elements normally are of low concentrations in natural environments. Unfortunately, insufficient experimental and observational data are available to ascertain heavy metal behaviour during neutralization of acids by cation exchange. For example, many metals including common non-toxic elements such as Ca^{++} and Na^+ are present on exchange sites of clay minerals. If the heavy metals are bound more strongly to the exchange sites than are non-toxic cations, neutralization of acidic rainwater would result in release of Na^+ and heavy metals may remain bound on the clay surfaces.

In summary, some clay minerals have excellent acid neutralization capacities, whereas others such as kaolinite do not. If acidic rains penetrate surficial deposits, the clay mineralogy of the deposits first must be determined before its neutralizing power can be assessed. There is a distinct potential danger of heavy metal pollution of natural water courses if 'contaminated' clays are subjected to attack by acidic solutions.

2.2.2.5 Calcite

Calcite is the major mineral constituent of limestone and is a powerful neutralizing agent (reaction 1). Where limestones are abundant as bedrock, they should effectively neutralize acidic waters. However, limestones are generally restricted to regions where bedrock is of sedimentary origin such as southwestern Ontario and regions of western Canada. Where limestones are present in bedrock, they generally are also included as constituents of glacial debris, thus adding to the total capability to neutralize acidic rains. However, mineralogical studies of the debris would have to be conducted to determine the presence of limestone, because it certainly is not ubiquitous and may not be present in the glacial debris covering many parts of Canada. Calcite usually is not an abundant constituent of weathering profiles in temperate regions.

Calcite contains primarily Ca^{++} and no cations harmful to the environment should be released in quantities.

In summary, calcite and limestones are ideal agents with which to neutralize acidic waters. Where present in glacial debris or as bedrock, there should be minimal adverse consequences resulting from either acidic rainwater or from metals released as a result of calcite dissolution.

2.2.2.6 Other Minerals

The other groups of minerals which may be of importance in neutralization reactions are metal oxides, hydroxides, and sulphides. These generally constitute no more than about two per cent by weight of bedrock. Similarly, they are minor constituents of most glacial deposits, although metal oxides and hydroxides may constitute an appreciable portion of weathering profiles (Carroll 1970). Reaction of sulphides, oxides and hydroxides with acidic solutions at the earth's surface may be complicated and may proceed by any and all of the three reaction types. However, as they usually occur in small quantities, these minerals play quantitatively minor roles as neutralizers of acidic rain.

The sulphides are generally present in relatively unweathered bedrock and glacial debris and typically include elements such as Fe, Co, Ni, Cu, Zn, Pb, As, Hg, and other heavy metals (Deer et al. 1967). The oxides and particularly the hydroxides are much more abundant as weathering products. The hydroxides, found in weathered bedrock, glacial debris and in weathering profiles, are usually very finegrained and colloidal (Jackson 1964), and therefore have a large surface area to mass ratio. The large surface areas are conducive to transition metal and heavy metal adsorption (cation exchange). Under normal pH conditions, the hydroxides may adsorb these metals from solution. In fact, the bulk of these elements may reside on oxides and hydroxides of soil (Jenne 1968). When the mineral groups are contacted by acidic solutions, they will release these metals to solution (Murray et al. 1968). The neutralization probably proceeds by processes similar to reactions (2) and (3), although some hydroxides will dissolve by reaction (1).

To summarize, sulphides, oxides and hydroxides are present in small quantities in most bedrock and surficial deposits. Consequently, they will have limited neutralizing effects. The minerals contain transition metal ions, either within their lattices or adsorbed onto their surfaces. These will be released to solution by reaction with acidic solutions. Once released from the minerals, the fate of the metal ions is difficult to predict. The ions immediately may be removed from the waters by exchange onto clay minerals and organic materials for example, thus keeping them at low concentrations in solution. Alternatively they may remain in solution and possibly present a risk to the environment through their increased mobility and bioavailability. The behaviour of most transition metals in the complex natural environment is poorly understood.

2.2.3 Reaction Rates

The preceding sections reviewed mineral properties, neutralization reactions, and the types of ions released to solution. The rates at which reactions proceed are also of utmost importance. If a mineral has the capacity to neutralize acids (i.e., the mineral is a very strong base) but the neutralization reaction proceeds only slowly, then during periods of high acid input to an environment, the mineral may neutralize only an insignificant amount of acid. True acid-base reactions (reaction 1) generally are controlled by the rate at which the solid dissolves and may range from the scale of seconds to days. For example, the calcite from limestone dissolves rapidly, whereas other minerals such as iron and manganese hydroxides may dissolve much more slowly.

Mineral transformation reactions (reaction 2) generally proceed more slowly because the solid products formed by the reaction require time for organization of crystal lattices of the product minerals. The reaction rates generally range from the scale of days to years to thousands of years.

Cation exchange reactions (reaction 3) generally are very rapid, complete cation exchange often occurring in seconds and minutes (Burque et al. 1980). These reactions can rapidly neutralize large quantities of acidic waters. Cation exchange reactions, particularly on clay minerals of high exchange capacity, and calcite dissolution (acid-base reaction) probably are the two most important types of neutralizing reactions. Both proceed rapidly and have large capacity to neutralize acids. The clay minerals will rapidly release transition metals to waters during the neutralization process.

2.2.4 Contact Times and Permeabilities

Granitic and metamorphic bedrocks are impermeable except along fractures. Rainfall which does not enter fractures is removed to streams and lakes via surface drainage. When this occurs, there is little surface area exposed to contact and react with acidic rains. Furthermore, even if rainwaters migrate down fracture channels, there may be little reaction between acidic rainwaters and rock because the fracture surfaces are already altered, the rocks' basic constituents having been dissolved or neutralized by large volumes of normal (slightly acidic) rainwater. In such circumstances, even rock containing minerals with high capacities for acid neutralization (feldspars, micas, clay minerals and calcite) may be ineffective at neutralizing acids simply because they do not contact the solutions. These problems will be particularly acute in areas of the Precambrian Shield where many regions contain impermeable bedrock and little or no surface deposits (glacial debris or weathering profiles).

Sedimentary rocks generally have longer contact times and greater permeabilities since they are usually more porous. Therefore, much larger surface areas are available for neutralization of acidic rainwaters.

Glacial debris, which covers much of Canada, is heterogeneous but permeable zones generally are present. These serve as regions through which rainwaters and surface waters can percolate. As a result, large thicknesses of glacial cover may serve to neutralize acidic waters. Transition metals released to waters during neutralization may remain in solution, or upon neutralization may be removed by exchange (or adsorption) onto other surfaces. Again, there is limited information on transition metal behaviour in complex natural environments.

Weathering profiles are generally porous and permeable and some information is available on the behaviour of metal ions in these profiles (Nesbitt 1979; Kronberg _et al_. 1979; Nesbitt _et al_. 1980). As acidic waters migrate through soil profiles, the metal ions are leached from the soil minerals by acidic ground waters. The metals are transported from the upper portions of the profiles to regions containing minerals of significant neutralizing powers such as montmorillonite and illites. Upon neutralization of the acidic waters, the transported metals are removed from solution and exchanged back onto the montmorillonite and illite group minerals (Nesbitt 1979; Duddy 1980). Continued influx of acidic waters eventually exhausts the neutralizing capabilities of the montmorillonites and illites. Once the capability is lost, metals which were previously exchanged onto the clays will be leached by the acidic waters, transported further and deposited where the basic properties of the minerals have yet to be exhausted.

2.2.5 Summary

Clay mineral groups such as the montmorillonites and illites have reasonably high capacities to neutralize acids by mineral transformation reactions (reaction 2) and cation exchange reactions (reaction 3). Cation exchange on clays is rapid, so that these minerals can quickly neutralize acidic waters. These same clay minerals, however, retain transition metal ions which can be released to solution during neutralization.

Calcite has a high capacity to neutralize acids and reacts rapidly in doing so. Furthermore, it contains no appreciable quantities of transition metals. Bedrock and thick surficial deposits (glacial and weathering products) containing these minerals should provide a high buffering capacity in regions where they are found.

Feldspars, although having a high neutralization capacity, react by mineral transformation. The reaction is slow. The feldspars provide long-term (long lasting) buffering capacity whereas the clays are short-term.

Quartz and kaolinite provide no significant buffering capacity.

Regions of the Precambrian Shield, large areas of which are predominantly quartz plus feldspars containing no significant glacial cover or weathering profiles, are poorly buffered and highly susceptible to the effects of acidic precipitation. Areas containing thick surficial deposits and carbonates or shales in bedrock are much less susceptible. Knowledge of groundwater hydrology and the minerology and permeability of materials comprising a watershed is necessary in order to assess its sensitivity to acidification, although the interrelationships among these parameters are complex and have yet to be quantitatively described.

2.3 Surface Water Systems

2.3.1 Terrestrial Ecosystem

The terrestrial ecosystem influences the chemistry of precipitation as it passes through to become either surface water runoff or groundwater. The main pathways for transport of water in a lake's watershed are shown in Figure 2.3. The transport routes include groundwater flow through porous overburden and fractured bedrock directly into a lake or stream, surface water runoff, and snowmelt. The basic properties of groundwater and its interactions with the parent soils and bedrock are described in the previous section. The effects of the watershed upon groundwater discharges and snowmelt are considered here. In this section, three overview approaches to analyzing the susceptibility of watersheds to acidification are presented. They are the use of mapping, hydrograph analysis, and material budgets for a watershed ecosystem. More detailed approaches (including topography) may be used, but they are viewed in this report as refinements to the more general approach.

2.3.1.1 Susceptibility Based Upon Geological Mapping

Based upon knowledge of bedrock geology, Galloway and Cowling (1978) mapped those areas of North America which are potentially sensitive to acidic precipitation (see Figure 2.4). The shaded areas indicate bedrock composed of igneous or metamorphic rock, whereas unshaded areas are calcareous or sedimentary rock. Igneous or metamorphic bedrock weathers slowly; therefore, lakes in these areas are assumed to have low alkalinity and low buffering capacity. Galloway and Cowling verified this assumption by compiling alkalinity data - lakes with low alkalinity were consistently found in regions having igneous and metamorphic bedrock.

Some care must be used with such mapping. Although it is a good indicator of regional susceptibilities, there are exceptions. For example, lakes such as Lake of the Woods and its embayments which are situated predominantly upon granitic rocks have moderate alkalinities. Glass and Louckes (1980) noted that there are areas in Maine underlain by granitic bedrock, suggesting a low buffering capacity where lakes have not become acidified despite receiving precipitation with an average pH of 4.3. It is believed that acidification has not occurred because drainage basins feeding these lakes contain limestone-bearing till and marine clay. Attempts to classify regions by sensitivity to acidic precipitation must, therefore, take into account the potential buffering capacity of rock mixtures, the types of soils overlying the rock formations, and the modifications by the terrestrial ecosystem. This aspect has been more recently expanded upon by Coker and Shilts (1979) and Shilts (1981) in their discussion of glacial dispersal of clay and carbonate bearing minerals and its consequence with respect to an area's sensitivity to acidic precipitation.

2.3.1.2 Susceptibility Based Upon Hydrograph Analysis

As suggested by Figure 2.3. a portion of stream flow will be from overland surface flow and a portion will be from groundwater flow. During and after a rainstorm, the stream flow will increase rapidly, and subsequently decrease. The record of this rise and fall is called a hydrograph. A generic hydrograph is sketched in Figure 2.5 together with two generic chemographs or records of the concentration of a substance in stream water over time corresponding to the hydrograph. Two chemographs are shown - one for a soluble substance and one for a particulate material. Only the one for a soluble substance will be considered here in detail.

As suggested in Figure 2.5(a), hydrological techniques exist for separating that portion of the hydrograph due to groundwater flow from that portion caused by surface runoff. Such techniques are called base-flow separation techniques. Chemical tracers have demonstrated that for some hydrographs, more of the hydrograph is actually caused by groundwater flow than estimated by base-flow separation techniques. This results from rainfall penetrating surficial tills and sending a gravity type shock wave through the groundwater. forcing more groundwater out than would occur, based strictly upon normal groundwater flow rates suggested by the lower line. Therefore. some question arises in blind application of such techniques and an alternative separation is suggested in Figure 2.5(a). Nonetheless, for a spectrum of hydrographs, a base-flow separation can be made fairly readily if stream flow rates are available from Water Survey of Canada data base. Use of a spectrum of hydrographs allows one to assess the effects of quantities and intensities of rainfall and the time of the year (spring snowmelt or a summer thunderstorm) upon the flow path of water through a watershed.

A curve for calcium or alkalinity would be typical of that shown in Figure 2.5(b). The first part of the curve represents the background concentration attributable to groundwater flows, or the net solubilization of materials due to all groundwater flow paths. The solid line represents the dilution effect of this groundwater by rainwater, assuming that all surface runoff crosses the watershed without picking up any more of the substance. Hence, the bottom line is a mass balance on the amount of the element in groundwater and in the rainwater. The dotted line represents the actual observed chemograph. The difference between the dotted line and the solid line represents the amount of material picked up by surface water runoff.

Analyses of a hydrogen ion and a pH chemograph are sketched on Figures 2.5(d)i and ii. (Two actual chemographs for springmelt and a summer thunderstorm are given on Figures 2.14 and 2.15, respectively.) The graph for hydrogen ion concentration is opposite to that for calcium or alkalinity shown in Figure 2.5(b), while that of pH is similar. The hydrogen ion concentration results from the fact that acidic rainwater is not entering groundwater flow, but rather is loading the stream with a hydrogen ion concentration higher than that of groundwater. The difference between the solid and dotted lines represents the amount of H^+ adsorbed by surficial soils.

Analyses of a spectrum of such chemographs allows one to estimate the amounts of material picked up by the watershed (H^+) or by the rainwater as a function of time of travel through the two main flowpaths (surface water, groundwater). When coupled with knowledge about the total acid neutralizing capacity of the two routes, this allows one to make statements concerning not only the susceptibility of the watershed to acidification, but also the rate at which the acid neutralizing capacity of the watershed is being used up.

An outline of this approach is presented here. A first essential piece of information is how much of the annual flow from the watershed occurs during winter and spring when groundfrost prevents significant groundwater infiltration. During this period, the effect of a watershed upon adsorption of acidity will be minimal. This effect is accentuated in certain types of watersheds - steeply sloped, non-forested watersheds will essentially not modify rainwater acidity at all during these time-periods. Only if significant acidity diffuses from snow into the soil burden will much of it be adsorbed. A second piece of information is the percentage of rainfall reaching a lake via surface runoff and through groundwater flow.

A third piece of information relates to the amount of neutralization occurring through each route and the rate of exhaustion of the acid-neutralizing capacity of the watershed. This is a function of the cation exchange capacity and other mechanisms for adsorbing acidity, the time of travel for water through the different groundwater pathways, and the time required for adsorption-desorption reactions.

2.3.1.3 Susceptibility Based Upon Analysis of Watershed Cycles and Material Budgets

Another approach to assessing watershed susceptibility is based on watershed cycles and material budgets. These are, at present, research tools requiring fairly detailed hydrological analysis and precise mass input-output measurements. The techniques are rapidly evolving so that, within five years, they should be useful as management tools for assessing susceptibility. Further, they describe the whole process of mitigation within a watershed due to weathering and terrestrial ecosystem cycles. They are presented here to provide a conceptual perspective and qualitative description of the type of management tool which will be available in the near future.

Weathering reactions act to adsorb acidity and to mobilize metals from the watershed. A conceptual sketch of a watershed's weathering reaction is given in Figure 2.6. It shows that acid inputs react with minerals such as primary silicates to form secondary minerals and to release basic cations. The process is amplified by internal terrestrial ecosystem cycles. These processes offer an approach of using an input-output budget from watersheds.

As an example, a material budget for 12 elements is given in Table 2.1 for Hubbard Brook in the Appalachian Mountains of New Hampshire. This is one of the most intensively studied watersheds in North America with a relatively high acidic precipitation input. Its terrain is fairly steep and is covered by a coniferous-deciduous forest which is estimated to be 55 years old on average since the last cutting. This area has an aggrading ecosystem, meaning that there is, at present, an accumulation of biomass in the forest.

Table 2.1 Summary of Annual Input-Output Budgets for Undisturbed Forested Ecosystems at Hubbard Brook(a)*

Element	Input, kg/ha.yr	Output kg/ha.yr	Net gain (+) or loss (-) kg/ha.yr
Si	-	23.8	-23.8
Ca	2.2	13.9	-11.7
Na	1.6	7.5	-5.9
Al	-	3.4	-3.4
Mg	0.6	3.3	-2.7
K	0.9	2.4	-1.5
Organic C	1484(b)	12.3	+1472
N	20.7	4.0	+16.7
Cl	6.2	4.6	+1.6
S	18.8	17.6	+1.2
H	0.96(c)	0.10(c)	+0.86
P	0.036	0.019	+0.017

(a) Input values for organic C, N, and S include bulk precipitation, estimates of aerosol impaction, and net gaseous uptake; all others are based on bulk precipitation only. Output values include both dissolved substances and particulate matter in stream water.

(b) Includes ecosystem biomass accretion (net ecosystem gaseous uptake of CO_2) based on the period 1961-1965 (Whittaker, et al., 1974); therefore output does not include respiration losses of CO_2.

(c) Dissolved form only.

* Adapted from Likens et al. (1977)

The bulk ionic composition of water entering the ecosystem is essentially a combination of acids such as H_2SO_4, HNO_3 and HCl. In contrast, the water leaving the system is characterized by neutral salts such as $CaSO_4$, Na_2SO_4, $Mg(NO_3)_2$, and to a lesser extent by chlorides and bicarbonates. The rate at which chemical weathering proceeds may be determined by using "the rate at which cations are withdrawn from the system" as a parameter. The main water outflow is via surface streams; groundwater outflow is minimal because the bedrock is composed mainly of highly metamorphosed sedimentary rocks (mudstones and sandstones) and granitic rocks. Surficial soils are 0.5 m or less in thickness, composed of an organic layer and well-drained podsols of sandy-loam texture. The inorganic soils are derived from glacial erosion and weathering of the metamorphic bedrock. Most precipitation infiltrates because of the soil's highly porous nature and the rough regional topography (pits and mounds formed by wind-thrown trees). There is little overland flow. Water leaves the watershed via surface streams, and not via groundwater flow regimes due to the "tightness" of the underlying bedrock. Accordingly, the main water route is rainfall, infiltrating to become groundwater, flowing to the surface streams and then out of the watershed.

The input-output material budget (rainfall-stream outflow) shows that a net acid (H^+) input of 0.86 kg/ha-yr (0.86 kilo moles/ha-yr; 0.86 kilo equivalents/ha-yr) causes a net cation release of 49 kg/ha-yr (1.7 kilo moles/ha-yr; 4.9 kilo equivalents/ha-yr). Chlorides and sulphates are approximately conservative (within measurement error); that is, what enters the watershed leaves the watershed. Major nutrients (carbon, phosphorus and nitrate) are accumulated by the ecosystem. This budget shows that sulphates or nitrates cannot be used as indicators or fingerprints of the behaviour of acidity (H^+) in watersheds. This is in contrast to atmospheric water chemistry, in which sulphate and nitrate concentrations are used to estimate the concentration of H^+ for many rainfall events. These numbers show that there is a large release of cations, but a minimal release of anions and alkalinity in the form of bicarbonate from such a watershed. Hence, even though such watersheds weather and adsorb most of the acidity input to them, their lake waters are susceptible to acidification due to direct atmospheric acid inputs to the lake and due to the very slow (if any) release rate of any alkalinity from the watershed to the lake.

These input-output numbers do not by themselves represent the actual internal cycles. The calcium and sulphate cycles are illustrated in Figures 2.7 and 2.8, respectively (Likens et al. 1977). Similar cycles are not given for H^+; rather, five major pools between which elements cycle are described: above ground living biomass, below ground living biomass, forest floor (deadwood, litter and upper organic layers of the soil), mineral soil and rock, and available soil elements (estimated from soil depth, density and element analysis). An arbitrary depth of 0.45 cm was assumed for the mineral soil, and this appears to be the depth within which most active soil processes occur. The rock content assumes a given depth of rocks; the mineral content of the rock is known and measurements show that 1500 kg of rock are weathered each year in the watershed.

Overall, the flux of calcium or sulphur between the major pools is larger than the atmospheric input or discharge. For example, considering above and below ground biomass losses to the forest floor and soil, the fluxes for Ca and S are 51 and 27 kg/ha-yr. These values are, respectively, 3.7 times and 1.5 times the hydrological export. These figures show that the effect of a terrestrial ecosystem is to cause internal fluxes which are higher than input or output fluxes. A portion of these internal fluxes is then lost through export while the losses are made up from internal sources due to weathering of bedrock and atmospheric inputs.

The sulphur cycle illustrates the problem with trying to use sulphur as a fingerprint for lake acidification. For two Swedish lakes, the cumulative atmospheric sulphate loading to a lake has been correlated with the resultant pH. The results shown in Figure 2.9 indicate that a sharp drop in pH occurs past the lake's threshold. Also past this point, it is more likely to show large fluctuations in response to episodic additions. These kinds of curves have allowed some researchers to attempt to explain lake susceptibility on the basis of sulphate loading. Such curves are useful where the buffering capacity is known, where the watershed does not remove much H^+ from the rainwater, or where the majority of the lake's hydrological budget is composed of direct precipitation. Where the watershed significantly adsorbs acidity but not sulphate, such an approach may be quite erroneous for assessing lake susceptibility.

A description of the less extensively studied experimental watersheds in Canada for which data is currently being collected may be found in NRCC (1981).

2.3.2 Lake Water Chemistry

The chemistry of lake and stream water may be viewed as a large-scale chemical titration experiment with an endpoint. As rain falls on the watershed, its acidity is neutralized to varying degrees by the terrestrial ecosystem and geology (principally chemical weathering and ion exchange) of the watershed; the amount of neutralization depends on its flow path (surface runoff or groundwater runoff). Upon entry into a lake, the chemistry of the different streams and direct rainfall mix together. The mixture is modified by internal lake processes to produce the observed lake chemistry. Overall, it is expected that the dominant influence upon lake acidity will be the acidity of inflowing streams, rainfall and groundwater flow, with internal self-compensating mechanisms within the lake being of subsidiary importance.

2.3.2.1 Susceptibility Characteristics Given the Chemistry of the Lake Waters

The susceptibility of a lake to acidic precipitation must be viewed from a watershed-lake perspective, rather than strictly from a lake perspective. However, an analysis of the water chemistry can allow initial inferences to be made about the susceptibility of the lake to acidic rainfall.

Three approaches, none of which are mutually exclusive, have been evolving for assessing susceptibility based upon analyses of lake or stream water chemistry. They are: (1) calcium carbonate saturation indices; (2) alkalinity-conductivity-pH relationships; and (3) alkalinity titration curves. This represents a continuum from very general relationships for many lakes to very precise relationships for one lake.

Calcium carbonate saturation relationships are usually formulated in terms of indices. Three particular indices are relevant for questions related to drinking waters supplies - the Langelier Index (LI) the Calcite Saturation Index (CSI), and the ASTM 500 index. The LI was derived by Professor W.F. Langelier, a Sanitary Engineering Professor at the University of California at Berkeley, in the mid-1930s as an indicator of scaling potential in water distribution systems, water treatment plants, and cooling water systems (Langelier 1936, 1946). It is defined as:

$$LI = pH - pH_S \tag{1}$$

where pH is the measured pH and pH_S is the pH at which calcite ($CaCO_3(S)$) would start to precipitate for the given concentrations of calcium and carbonate. At very low ionic strengths (typical of many fresh waters), and 25°C, pH_S is defined as

$$pH_S = 11.26 - \log_{10}\left[Ca^{2+}\right] - \log_{10}\left[ALK\right] \tag{2}$$

where $\left[Ca^{2+}\right]$ is the concentration of calcium in mg Ca/L and $\left[ALK\right]$ is the alkalinity concentration in units of mg $CaCO_3$/L.

The water is at equilibrium when LI is 0, oversaturated (scaling occurs) when LI is positive, and undersaturated (corrosive or aggressive) when LI is negative. This index has found wide application as an index of scaling-corrosion potential in the municipal water supply industry.

The CSI was originally developed by Professor J.R. Kramer, a Geology professor at McMaster University (Kramer 1977) to examine the saturation characteristics of lake water. It is defined as:

$$\begin{aligned} CSI &= PI - pK_s \\ PI &= pK_2 - 2\log_{10}\left[ALK\right] - pH + 4.6 \\ pK_2 &= 10.618 - 0.015\,T \\ pK_s &= 8.02 + 0.0128\,T \end{aligned} \tag{3}$$

Here PI is the ion production of $\left[Ca^{2+}\right]$ and $\left[CO_3{}^{2-}\right]$, pK_s is the solubility product of Ca^{2+} and $CO_3{}^{2-}$, pK_2 is the second ionization constant of carbonic acid ($K_2 = \left[CO_3{}^{2-}\right]\left[H^+\right]/\left[HCO_3{}^-\right]$, and $pK_2 = -\log_{10} K_2$), and T is the temperature of the water. The CSI compares the ionic production of $\left[Ca^{2+}\right]\left[CO_3{}^{2-}\right]$ to its solubility product (the concentration of $\left[Ca^{2+}\right]$ and $\left[CO_3{}^{2-}\right]$ required to just cause the precipitation of calcite). If the CSI is negative, it is supersaturated, if the CSI is positive, the water is undersaturated.

The ASTM 500 index (developed by the American Society for Testing and Materials) is defined as:

$$pH + \log_{10} (\text{total alkalinity} \times \text{calcium hardness})$$

where total alkalinity and calcium hardness are expressed in mg $CaCO_3/L$.

This index is used by the Pollution Control Branch of the Ontario Ministry of the Environment to describe corrosivity of water supplies. A value of <10 is very corrosive, 10-12 is moderately corrosive and >12 is not corrosive.

These three indices express similar relationships, although they consider different entities. They do not directly express the susceptibility of lakes to acidic precipitation, but it is probable that "corrosive" concepts can also be extended to include susceptibility concepts.

In an overview examination of ASTM 500 indices provided by the Ontario Ministry of the Environment for municipal water supplies in Ontario, it was observed that water supplies in the Canadian Shield generally have index values of <12 and often have values of <10, whereas municipalities using well buffered water sources have higher index values.

Using the CSI, Kramer (1977, 1978, 1979) has mapped northern and eastern Ontario based upon extensive stream water sampling (Figure 2.10). Where the CSI is less than one, terrain is most stable and not susceptible to change; where it is between one and two, the terrain is possibly susceptible to change; where it is between two and three, the terrain is probably susceptible to change; and where it is greater than three, the terrain is susceptible to change. It can be seen in Figure 2.10 that several areas are identified as being susceptible to change.

There are some limitations in this work. The exact nature of the sampling frequency is not given by Kramer; several samples over the course of a year are needed if an integrated value of the CSI is to be obtained. In addition, the CSI will vary somewhat from year to year depending upon the magnitude and intensity of rainfall and the pathways for water movement to streams and lakes (groundwater, surface water, snowpack).

Correlations between pH, alkalinity and specific conductance within a lake water or stream water reflect the similarity of mechanisms governing the pH of inflowing waters to the lake. Kramer (1977) and Zimmerman and Harvey (1979) present scattergrams of various relationships. Kramer's scattergram of alkalinity and pH is given in Figure 2.11. Based upon estimates of lake water being susceptible to acidification, at certain alkalinities, a three-fold classification is given. He suggests that lakes in contact with $CaCO_3$ will have a high pH (8) and alkalinity (100 mg $CaCO_3$/L) and will be modified not by atmospheric loadings but only by extreme surface contamination. Lakes not in contact with $CaCO_3$ will have lower pH (6.5) and low alkalinities (25 mg $CaCO_3$/L), and are readily modified by atmospheric and land loadings. Lakes with inputs that are influenced particularly by subsurface lithology containing calcite would approach a simple $CaCO_3$-H_2O dilution model. The saturation line given in Figure 2.11 describes those waters that have been in contact only with $CaCO_3$ and have dissolved the calcite minerals to varying degrees. Lower concentrations of alkalinity and pH along this line reflect lakes whose dominant inflows arrive through non-calcareous pathways. Departures from this line arise from equilibrium with various other minerals (e.g., alumina silicate or clay minerals), weathering reactions, and atmospheric loading.

A test of the simple $CaCO_3$ dilution model is to assume that the specific conductance is determined by the Ca^{++} - HCO_3- system. From this assumption, theory gives the relationship

$$ALK = (-0.011 + 0.00909\ J)\times 50 \qquad (4)$$

where J is the specific conductance (umho/cm, 25°C) and alkalinity is in mg $CaCO_3$/L. A comparison of observations on various lakes with the theoretical relationship (Figure 2.12) shows that many Sudbury and Northern Ontario lakes follow this relationship well. For those that depart from this relationship (lower corner of graph), some other factors (other minerals, atmospheric loading) are controlling the relationship. These are the same lakes (Figure 2.11) where the carbonate alkalinity approaches zero and the residual alkalinity is 5 mg $CaCO_3$/L (0.1 meq/L). Substances which can impart this residual alkalinity include substances which behave as weak acids with a dissociation constant of pK = 4-6, such as particles in suspension (Fe and Mn oxides, clay minerals), ammonia, and organic acids. Adsorption reactions can occur between H^+ and the suspended matter, causing the suspended matter to appear as residual alkalinity.

Another more precise method to determine the system controlling pH and the susceptibility of waters to acidification is titration with acid under a N_2 atmosphere (to prevent atmospheric invasion of CO_2) combined with a Gran analysis to determine whether the bicarbonate system is governing the determination of alkalinity, or if some other substance is significant (see Appendix A for details).

A comparison of alkalinity titration curves for a soft-water lake and a hard-water lake is shown in Figure 2.13 (Zimmerman and Harvey 1979). The slope of each line is a measure of the buffering capacity at a given pH. The relative slope gives an indication of the ability of the two waters to resist acidification and hence is an indicator of the relative ability of the two watersheds to maintain this capability. If the alkalinity titration curve is dominated by the bicarbonate system, one is able to use the lake's alkalinity as a first coarse cut at determining susceptibility, as in Figure 2.12. Lakes low in alkalinity which may or may not be dominated by the bicarbonate system, are the most likely candidates for being susceptible to acidification. It is suggested that these would represent a priority for assessing susceptibility of water supplies. Since alkalinity data are conventionally available for most current water supplies, such a data base could be used for examining the susceptibility question.

For this reason, Zimmerman and Harvey (1979) proposed that pH, alkalinity and conductivity be used as triangulatory parameters for determining acid sensitive lakes. It is desirable to use mass balance analyses and to incorporate major cations in statistical relationships to determine the susceptibility of lakes to acidification. However, such detailed relationships require detailed data which at present are only evolving. For these parameters, they suggest lower limits for non-susceptibility of: alkalinity - less than 0.300 meg/L (15 mg $CaCO_3$/L); conductivity - less than 30-40 µmho/cm; and pH - less than 6.3 to 6.7. The three parameters are deemed useful because of the decrease in contribution of alkalinity to conductivity for conductances of less than 30-40 µmho/cm and because of the uncoupling of pH from alkalinity at about 6.3. However, because alkalinity (irrespective of source) represents the actual acid neutralizing capacity, and variations in lake water alkalinity are more easily explained, alkalinity is suggested to be most useful as a single master variability for assessing susceptibility.

2.3.2.2 Lake Processes

The susceptibility of a lake water to acidification cannot be assessed strictly by considering the inflow volume of water and its alkalinity. Physical processes and biochemical mechanisms can mitigate and change the rate of acidification.

A prime physical process of concern is the timing of spring runoff compared to timing of spring overturn (if it occurs). Figure 2.14 shows the inflow rate and pH of a stream entering a Canadian Shield lake near Dorset, Ontario during spring runoff. It has been shown that up to 80 per cent of the hydraulic and chemical loading to a lake can occur during this period, particularly in headwater lakes. The increase in acidity with increasing flow rate appears to be caused by the accumulation of H^+ in snow and the subsequent spring snowmelt; its exact cause is still not known. During this period of time, the stream water has a temperature of 0-1°C and the lake is ice covered. Since the stream water typically is lighter than the colder, denser lake water, it will flow across the lake's surface under the ice to the lake outflow. This behaviour causes a large portion of influent acidic waters to pass through the lake without affecting or being affected by its buffering capacity.

After the ice is out, a substantial portion of the total hydrograph inflow may enter the lake. If vertical wind mixing does not occur, surface heating will complicate the interaction of stream inflow with lake waters; however, the inflow will probably pass through the lake without significantly affecting or being affected by the lake water.

During summer stratification of the lake, sharp intense thunderstorms can cause a pronounced increase in acid input to the lake (see

Figure 2.15). Such inputs may pass through the lake without affecting its chemistry substantially; however, if the epilimnion occupies much of the lake volume, the effect of the input would be felt fully by the lake.

Biochemical mechanisms influencing acid neutralization include residual alkalinity, net phytoplankton production, decay of inflows of organic carbon, chemical precipitation within the lake water column and ion exchange of H^+ with suspended matter. The ability of lake alkalinity to absorb acidity has been described previously. The effect of net phytoplankton production upon lake acidity is illustrated by the Redfield Equation (Stumm and Morgan 1970).

$$\underset{\text{1 mole of algae}}{C_{106}H_{263}O_{110}N_{16}} + 138O_2 \underset{\text{Production}}{\overset{\text{Decay}}{\rightleftharpoons}} 106\ CO_2 + 16\ NO_3^- + PO_4^{3-} + 122\ H_2O + 19\ H^+ \tag{5}$$

It describes an inferred stoichiometry of the major relationships involved in the formation (photosynthesis) and decay (respiration) of oceanic algae.

The Redfield Equation suggests that for each mole of algae produced, 19 moles of H^+ are removed from the lake water. Hence, algal formation and settling in lakes represents a sink for hydrogen ions. While this equation is for planktonic algae, attached algae and rooted aquatic macrophytes will act in a similar fashion.

Alternatively, a source for acid production in lakes is the decay of organic matter, which produces various elements from the organic substrate, including H^+.

Chemical precipitation of major ions within the lake can be a mechanism for addition of bicarbonates to the lake. Schindler _et_ _al_. (1980) have demonstrated this process in their experiment which involved adding sulphuric acid directly to a lake near Kenora, Ontario. The lake pH decreased only 31 to 38 per cent as much as predicted. It was suggested that bacterial reduction of sulphate in the anaerobic hypolimnion resulted in CO_2 respired by the decomposers to be accumulated as bicarbonate (HCO_3^-). Ferrous iron (Fe^{2+}) apparently evolved from the sediments because of anaerobic conditions, precipitated with S^{2-} as vivianite (FeS) and settled. The interpretation is somewhat suspect as CO_2 respired by decomposers would react with H_2O to form H^+ and HCO_3^-. The H^+ could exchange with Fe^{2+} from the sediments to maintain a complete charge balance. However, this is definite evidence for the ability of lakes to sequester acidity from its waters.

Inputs of humic and fulvic acids and inorganic particulates provide sinks for H^+. Adsorption of H^+ onto such particulates is probable; ion exchange is also possible. The extent of these reactions depends upon the cation exchange capacity of the inorganics and the degree of ionization of the organics. The size of this sink depends upon the concentration of organics and inorganics, the rapidity with which exchange reactions occur, and the time that the particles remain in the water column.

2.3.2.3 Implications of Acidification for Other Water Quality Parameters

An extensive increase in the concentrations of certain trace metals has been associated with acidification. The origins of trace metals are threefold - direct atmospheric inputs, increased watershed release due to weathering reactions, and mobilization in the lake. The relative magnitude of each source is often difficult to discern.

In the Sudbury area, high concentrations of nickel, copper, and other trace elements in lakes surrounding the Sudbury stack have been attributed directly to the stack emissions. Emissions of trace metals are associated in many areas with coal burning in fossil fuel generating stations.

Watershed weathering acts to mobilize elements. Typical mobilization quantities are shown by data of watershed budgets (Likens et al. 1977). In particular, certain aluminum-bearing minerals are susceptible to leaching. Aluminum appears to be the primary element mobilized by acidic precipitation from soil horizons which would normally immobilize the elements, in regions characterized by soils with poor buffering capacity

(GCA Corporation 1980). The elevated levels of aluminum are correlated with depressed lake pH. Current toxicity work suggests that the elevated concentrations of aluminum cause toxic effects upon fish at levels of 0.3-0.5 mg Al/L.

Under anaerobic conditions, a decrease in pH was found to increase the manganese concentration in Lake Mendota (Hoffman and Eisenreich 1981). This was the result of $MnCO_3$ dissolution from the sediments.

For metals such as lead and mercury, elevated levels have been found in fish as a function of low pH (Ontario Ministry of the Environment 1981). Whether such elevated concentrations are due to increased mobilization from the lake sediments or to atmospheric inputs is unclear. Recent work suggests that with decreasing pH, lead and mercury are released from sediments as bacterially transformed, methylated species (Mayfield 1980). The concentrations of other metals, including zinc and cadmium, have been correlated with increased lake acidification (GCA Corporation 1980).

The effects of acidic conditions on aquatic microflora have been investigated in lakes near Sudbury (Thompson and Wilson 1975). Acidic lakes were found to support populations of heterotrophic bacteria and fungi that were similar to those observed in neutral lakes. However, another study (Weaver 1968) demonstrated significant species differences between an acidic stream (pH 3.0-4.1) and a control stream (pH 6.3-6.7). Fungi and yeast populations were more diverse in the acidic stream. In addition, several of the species observed have been implicated in cases of human infection and disease.

Microbial virulence, enterotoxin production, viral infectivity, and the efficacy of chlorination also vary with pH, with effects which are species-specific. In general, however, bacteria and protozoa populations decrease, fungal and yeast populations increase, and viruses are relatively resistant to acidic conditions (see Appendix B).

2.3.3 Summary

In summary, material budgets and internal fluxes are methods for determining ionic balances and electro-neutrality balances on watersheds. They quantify, in a fairly precise fashion, the actual relationships between atmospheric acidity and the ability of a watershed to mitigate (or adsorb) the acidity, or to release substances capable of adsorbing acidity in the lake (humic acids, inorganic particulates and alkalinity such as bicarbonate ion). They are, at present, mainly research tools. Accordingly, it is suggested that geological mapping and analyses of lake water chemistry first be used to determine lake susceptibility. Computations of total acid neutralization capacity of the watershed can then be made. Sample input-output watershed budgets can be constructed for specific lakes and compared to the total acid neutralizing capacity of the watershed. In this way, the susceptibility of an individual lake can be estimated. For lakes which are quite susceptible, it is suggested that input-output watershed budgets be measured to verify the degree of susceptibility and to further quantify the rate at which acidification will occur.

3. APPLIED ASPECTS

Those factors within a watershed which contribute to the sensitivity of the catchment basin to acid rain have been discussed previously. The effects on drinking water supplies of public health concern are: (1) decreased pH at a water supply intake, leading to a potential corrosion problem within the distribution system itself. This corrosion problem could lead both to costly damage in the distribution system and to the release of potentially toxic constituents such as trace metals and asbestos from structural components of the system; (2) acid deposition, together with the associated elemental and organic contaminants or substances leaching from the watershed, resulting in levels of chemical constituents in excess of drinking water guidelines recommended by Health and Welfare Canada (1978); or (3) a combination of altered pH and chemistry, leading to a change within the water supply system which may cause public health concern related to biological pathogens (see Appendix B).

The sensitivity of a water supply or catchment basin should not be viewed as constant. As discussed, catchment basins have time-varying abilities to 'neutralize' the effects of acid deposition. Catchment basins with deep, permeable, carbonate-rich glacial debris, low relief, and a low ratio of water surface area to total catchment surface area are generally expected to be relatively insensitive; those catchment basins with shallow, silicate-rich soils overlying granites or silica sandstones of low permeability, high relief, and a high ratio of water surface area to total catchment surface area are expected to be very sensitive. Although the waters from each of these insensitive and sensitive types may be similar in terms of pH at one point in time, the former has a very large buffering or neutralization capacity, whereas the latter has a very small buffering or neutralization capacity. Accordingly, the sensitive catchment areas are those which will show the most marked, rapid, and possibly irreversible changes if acid deposition continues into the future.

In order to carry out a thorough assessment of a water supply or catchment basin, it is necessry to assemble information related to the theoretical factors discussed in Section 2. This would enable a summation of the contributing factors which control sensitivity, and would consequently allow a prediction of the likelihood of change.

At present, however, this level of information is available for only a few, well-instrumented and sampled research watersheds. More detailed, long-term studies will be necessary to define many of these parameters for major Canadian water supply catchment basins.

In the absence of site-specific data, inferences can be drawn from a knowledge of existing, seasonal water chemistry within the watershed, general bedrock maps of the area, and acid rain isopleths. These inferences, when coupled with hydrographic data and knowledge of other general watershed variables, allow an estimate of sensitivity to be made.

On a coarser scale, general bedrock maps of the country which are overlain by acid rain isopleths allow a very rough approximation of sensitivity to be made.

In this section, the sensitivities of several community water supply systems are approximated, using a combination of general bedrock or glacial debris mineralogy and water chemistry where available. Bedrock and glacial debris are first considered for their content of carbonate minerals and montmorillonite clays; surface waters are evaluated for their alkalinity.

The municipalities of Winnipeg, Huntsville and Saskatoon were selected to represent cases of intermediate, high and low sensitivities to acidification, respectively. The sensitivities of their water supplies are analyzed in detail and are summarized in the following sections (3.1-3.3).

3.1 Winnipeg

The City of Winnipeg derives its water supply from Shoal Lake, an embayment of Lake of the Woods. In the first stage of the evaluation, overview data for the catchment basin are summarized from the Hydrological Atlas of Canada.

Annual precipitation	650 mm (estimated pH 4.6-5.0 from Figure 2.1)
Annual snowfall	160 mm
Evapo-transpiration	500 mm
Annual runoff	150 mm
Water hardness	0-60 mg/L $CaCO_3$ (0-1.2 meq/L)
Turbidity	0-5 Jackson turbidity units
Total dissolved solids	0-50 mg/L
Bedrock - fractured igneous and metamorphic rock	low buffering capacity

These data, in particular the low buffering capacity of the regional bedrock, the low regional calcium carbonate hardness and alkalinity, and the slightly acidic rainfall, suggest that the water supply may be sensitive to the effects of acidic precipitation. As discussed in Section 2, bedrock of this type is sensitive; waters with an alkalinity of less than 0.3 meq/L or 15 mg/L $CaCO_3$ are classed as sensitive. Since this water supply is potentially sensitive based upon a first approximation, a more detailed review is required.

The second stage requires site-specific data from the water supply itself. A review of data (1974) from Shoal Lake, the raw water supply, shows the following water quality:

	Avg.	Max.	Min.	Limit for sensitivity classification
Water hardness (mg/L)	74	84	67	less than 15 mg/L
Specific conductance	159	171	137	less than 40 mg/L
pH	7.7	7.9	7.6	less than 6.3

The site-specific data suggest that, although this water supply is in a region that is broadly classified as potentially sensitive, the actual water supply was not (in 1974).

A more detailed review of the site-specific surficial and bedrock geology shows the north side of the catchment basin overlain by a silty to sandy till (Ontario Department of Lands and Forests Map S165 Kenora-Rainy River - Surficial Geology). Although its mineralogy is not given, the relatively high alkalinity is suggestive of some carbonate minerals in the till. The amount of buffering capacity, however, is unknown. The southern section of the catchment is covered by varved clay and silts. It is also reasonable to suppose that the clays contain some cation exchange capacity and are capable of neutralizing acidity and adsorbing metals to some degree. The thickness of the tills is generally less than one metre; the varved silts and clays vary from one to ten metres in thickness.

The bedrock structure of the area is quite complex (Ontario Department of Lands and Forests Map 2115 Kenora-Fort Francis sheet) but is of some importance in evaluating sensitivity because of the relatively thin cover of glacial debris on the north side of the lake. The major buffering minerals are found in the deposits of shale, dolomite, limestone and marble found within the catchment basin. The granites and volcanics also found in the area offer very little in the way of buffering capacity.

The thin, permeable tills probably allow significant groundwater contact with the neutralizing bedrock in localized areas. Accordingly, the bedrock in this area provides a long-term buffering capacity if acidic loadings are not excessive. The water supply would, therefore, be classed on the basis of the bedrock geology as relatively insensitive in the long term.

The relatively flat topography and suggested high capacity for rainfall infiltration through the sandy to silty tills also suggest that a drastic change in pH is not likely in the short term. The shallow depth of till and the relatively large water surface area to total catchment surface area, however, are factors which will make the water supply more sensitive with time and continued acid input. Similarly, the varved silt or clays on the south side of the catchment suggest a relatively low permeability and potential for significant spring runoff. This factor may result in a spring runoff of high acidity.

In summary, the catchment basin for Shoal Lake, which is the City of Winnipeg's water supply, shows mixed sensitivity characteristics.

1. Gross mapping shows:
   - (a) acidic precipitation pH, 4.6-5.0 (1979);
   - (b) regionally sensitive bedrock geology;
   - (c) low regional surface water buffering capacity.
2. More detailed mapping shows:
   - (a) a large water surface area to catchment surface area ratio;
   - (b) relatively low surface relief in the watershed;
   - (c) high permeability tills on the north side of the catchment;
   - (d) low permeability varved silts and clays on the south side of the catchment;

(e) potentially significant water inflow from Lake of the Woods, which is a more sensitive area[1];

(f) regionally mixed bedrock buffering capacity;

(g) 1974 water chemistry data which suggest considerable buffering capacity and no immediate concern.

As a check on the validity of this assessment, the key parameters of pH, alkalinity, hardness and conductivity should be reviewed over time. Our analysis suggests that acidity of the water supply is not a priority concern although this supply has enough sensitive features that it requires monitoring. The following table shows variations in key water quality parameters during the late 1960s and early 1970s.

	YEAR								
	1967			1971			1974		
Parameter	Avg.	Max.	Min.	Avg.	Max.	Min.	Avg.	Max.	Min.
pH	8.4	8.6	8.1	7.9	8.2	7.7	7.7	7.9	7.6
Conductivity µmhos/cm				165	181	146	159	171	137
Alkalinity $CaCO_3$ mg/L	76	84	69	74	76	68	72	81	62
Hardness $CaCO_3$ mg/L				78	87	72	74	84	67

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1. Coarse hydrological analyses suggest that the Shoal Lake Drainage Basin contributes 4 m^3/s to Shoal Lake whereas the city withdraws 3 m^3/s. This would normally suggest net outflow from Shoal Lake to Lake of the Woods. During summer periods, flow from the Drainage Basin is much lower, meaning that net inflow from Lake of the Woods occurs. Significant exchange flows between Lake of the Woods and Shoal Lake during the passage of storm fronts provide a second probable mechanism for inflow of water from Lake of the Woods.

These data indicate the possibility of a shift toward lower pH and alkalinity but, are insufficient to say whether or not the trend is significant. The data do, however, suggest that the water supply does require future monitoring and a more complete and up-to-date review based upon fundamental principles and actual water chemistry.

3.2 Huntsville

The Town of Huntsville derives its water supply from Lake Vernon on the Canadian Shield in south-central Ontario. Following the same methodology as applied to Winnipeg, an overview of the data for this area shows the following:

Annual precipitation	Approximately 900 mm (estimated pH approx. 4.3 from Figure 2.1)
Annual snowfall	Approximately 250 mm
Annual runoff	400-500 mm
Water hardness	0-60 mg/L $CaCO_3$
Turbidity	0-5 Jackson turbidity units
Total dissolved solids	51-150 ppm
Bedrock - igneous and fractured metamorphic rock	low buffering capacity

The above data show a relatively high level of sensitivity in this area. The pH of the precipitation is quite acidic, and the annual snowfall may result in a slug of acidic water entering the water supply in the spring. The low buffering capacity of the bedrock (Figure 3.1) suggests there is not much potential for neutralization of acidic seasonal surface waters from deep local or regional groundwater flow. Similarly, the low water hardness suggests there is little buffering capacity added to the system from surficial soils and glacial till. This town, like Winnipeg, also has a water supply potentially sensitive to acidification. A more detailed review, therefore, is warranted.

More site specific data, in particular, key water quality parameters in Lake Vernon, are available (Ontario Ministry of Environment 1979). The relevant 1979 data are:

	Avg.	Max.	Min.	Limit for sensitivity classification
Water hardness $CaCO_3$ mg/L	9	14	5	less than 15 mg/L
Specific conductance µmhos/cm	42	43	39	less than 40 mg/L
pH	6.9	7.9	6.4	less than 6.3

These data suggest that the water supply may be generally classed as sensitive to acidification.

The water supply lies in the Huntsville landscape unit and the Lake Vernon watershed contains five land units according to the Ontario Land Unit classification. A large part of the watershed consists of moderately broken uplands, with shallow surficial sands ranging from coarse to fine to silty in texture. The remainder of the catchment basin is weakly broken plains with deeper fine to coarse sands. Although mineralogical data are not available in the land classification, other data (Figure 3.2) show that the glacial and post-glacial surficial sediments are of a high sensitivity to acidic precipitation (United States-Canada Research Consultation Group 1980). Smaller watersheds feeding into Lake Vernon arise in a variety of areas from peaty marshes or swamps to areas of bare bedrock outcrops interspersed with varying depths of coarse to silty sands. There is no evidence in the drainage basin of any significant quantity of bedrock or surficial material with any major buffering capacity.

The relatively permeable nature of the surficial sands suggests that the spring runoff will be somewhat subdued and much of the water will be supplied via weakly buffered groundwater flow. The water surface area to total catchment surface area ratio is much lower than for Shoal Lake. Consequently, a higher percentage of the water in Lake Vernon has had some contact with surficial or bedrock geological materials, although the material has an inherently low buffering capacity.

In summary, the catchment basin for Lake Vernon, which is the Town of Huntsville's drinking water supply, shows a trend toward the sensitive side.

1. Gross mapping shows:
   - (a) acidic precipitation pH 4.3;
   - (b) regionally sensitive bedrock geology;
   - (c) low regional surface water buffering capacity.

   This suggests that a more detailed review is necessary.

2. More detailed mapping shows:
   - (a) a small to moderate water surface area to catchment surface area ratio;
   - (b) a moderate to high surface relief in parts of the catchment surface area;
   - (c) high permeability of surficial deposits in the catchment;
   - (d) low bedrock buffering capacity and suspected low surficial deposits buffering capacity;
   - (e) a 1979 water chemistry which shows a low buffering capacity and neutral to slightly acidic pH.

As a check on this sensitivity evaluation, a review of historical water chemistry is warranted. However, with the exception of conductivity, the key parameters necessary to evaluate the sensitivity of the water supply (pH, alkalinity, hardness) are not within the Ontario Ministry of the Environment data summary. In the absence of these data, the water supply should be classed as sensitive and monitoring programs instituted to determine if public health hazards exist.

3.3 Saskatoon

The City of Saskatoon derives its water supply from the South Saskatchewan River as it flows through the city. This example differs from the previous two, in that the effective catchment area is very large. Therefore, the data with respect to watershed bedrock and surficial geology, and general climatic variables are of a more general nature. The very large catchment basin also allows for levelling of spring runoff effects and resultant discrete chemical pulses. Following the same methodology:

Annual precipitation	400-1000 mm (5.5-6.5 pH from Figure 2.1)
Annual snowfall	120-400 mm
Annual runoff	5-1000 mm
Water hardness	120-180 mg/L $CaCO_3$
Turbidity	10-20 Jackson turbidity units
Total dissolved solids	151-300 mg/L
Bedrock - flat-lying sedimentary rocks	high buffering capacity

The data suggest that the water originating in the catchment basin of the South Saskatchewan River is relatively insensitive to the effects of acidic precipitation. The relatively high pH of the precipitation (above the 5.6 for normal rain) suggests neutralization of natural and man-induced acidity by prairie dust before precipitation reaches the ground.

The site-specific data from the South Saskatchewan River at Saskatoon confirm the above evaluation (Fisheries and Environment Canada 1977). These data are as follows:

	For 1968-1975			
	Avg.	High	Low	Standard Deviation
pH		8.7	7.4	
Conductivity µmhos/cm	397	494	304	33
Alkalinity $CaCO_3$ mg/L	141	165	115	9
Hardness $CaCO_3$ mg/L	170	195	121	13

All these data indicate that the water supply is generally insensitive to the effects of acidification. It therefore has a low priority for detailed review.

3.4 Sensitivity of Water Supplies to Acidification for Selected Canadian Cities Having Over 100 000 Inhabitants

The purpose of this section is to comment on the vulnerability of some of the largest cities in Canada to the effects of water supply acidification.

The first step in order to achieve this goal was to gather data for each city on general geology (bedrock, surficial deposits and their buffering capacity) and on the average pH of precipitation for the region. Information on geology for eastern Canada was drawn from Figures 3.1 and 3.2. For the Prairies and British Columbia, geological information (bedrock only) was taken from a map (#1250A) of the Geological Survey of Canada (1972). Information on the surficial deposits (soils) in the Prairies and British Columbia was derived from Clayton _et_ _al_. (1977). All data concerning the pH of precipitation were drawn from Figure 2.1. This information allowed the determination of buffering capacity of the water supply watershed for each city.

The second step consisted of gathering data on the raw water supply of these cities. Water hardness, alkalinity, specific conductance and pH were the parameters considered. By comparing the values obtained for these parameters for each city with the limits defined for sensitivity classification, an assessment was made of the sensitivity of each water supply to acidification.

The values for each parameter were obtained in most cases from the municipalities themselves. In Ontario, however, Ministry of the Environment regional offices provided the required information. When possible, values (average, maximum and minimum) were obtained for 1980. In some cases it was possible only to obtain an average value for each parameter for 1980 and in others only earlier data were available.

From the data given in this section, it is concluded that Halifax and Greater Vancouver are two cities where both the region and the water supplies are classified as sensitive to acidification. The other water supplies considered are not classified as sensitive. It is worth noting that most of these cities receive acidic precipitation, with a mean annual pH as low as 4.1 (Oshawa and St. Catharines).

Data on Surface Water Supply of Selected Canadian Cities Having Over 100 000 inhabitants

HALIFAX

Water supply	Pockwock Lake	
Regional Data		
Bedrock	granite, granite gneiss, orthoquartzite, syenite	low buffering capacity
Surficial Deposits	likely to be non-calcareous	low buffering capacity
Precipitation pH	4.4 - 4.6	acidic
Raw Water Supply Data	1980	

	Avg.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	8.8	less than 15
Alkalinity ($CaCO_3$, mg/L)	1.0	less than 15
Specific conductance (µmhos/cm)	40.0	less than 40
pH	5.1	less than 6.3

Conclusion

This water supply is located in an area broadly classified as potentially sensitive; moreover the water supply itself is classified as sensitive to acidification.

QUEBEC

Water Supply — Rivière St-Charles

Regional Data

Bedrock	limestone, dolomite and metamorphic equivalents	high buffering capacity
Surficial Deposits	high probability of occurrence of calcareous, fine-grained marine sediments	intermediate (or indeterminate) buffering capacity
Precipitation pH	4.2 - 4.3	acid

Raw Water Supply Data

1980

	Avg.	Max.	Min.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	24	30	17	less than 15
Alkalinity ($CaCO_3$, mg/L)	13	18	7	less than 15
Specific conductance (µmhos/cm)	49	151	67	less than 40
pH	7.0	7.3	6.7	less than 6.3

Conclusion

This water supply as well as the region in which it is located show low sensitivity to acidification.

LONGUEIL

Water Supply	Fleuve Saint-Laurent	

Regional Data

Bedrock	calcareous clastic rocks and carbonate rocks interbedded or interspersed with non-calcareous sedimentary, igneous and metamorphic rocks	intermediate-high buffering capacity
Surficial Deposits	likely to be calcareous	high buffering capacity
Precipitation pH	4.2 - 4.3	acidic

Raw Water Supply Data

1980

	Avg.	Max.	Min.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	127.2	140	114	less than 15
Alkalinity ($CaCO_3$, mg/L)	85.6	92	69	less than 15
Specific conductance (µmhos/cm)	330	360	303	less than 40
pH	8.12	8.52	7.84	less than 6.3

Conclusion

This water supply as well as the region in which it lies show low sensitivity to acidification.

LAVAL

Water Supplies	a) Rivière des Mille Iles b) Rivière des Prairies

Regional Data

Bedrock	limestone, dolomite and metamorphic equivalents	high buffering capacity
Surficial Deposits	likely to be calcareous	high buffering capacity
Precipitation pH	4.2 - 4.3	acidic

Raw Water Supply Data

1980

a) Rivière des Mille Iles

	Avg.	Max.	Min.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	42	48	38	less than 15
Alkalinity ($CaCO_3$, mg/L)	29	35	24	less than 15
Specific conductance (µmhos/cm)	Not available (N.A.)			less than 40
pH	6.9	7.2	6.8	less than 6.3

b) Rivière des Prairies

	Avg.	Max.	Min.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$ mg/L)	35	48	30	less than 15
Alkalinity ($CaCO_3$ mg/L)	23	29	18	less than 15
Specific conductance (µmhos/cm)	Not available			less than 40
pH	6.9	7.0	6.6	less than 6.3

Conclusion

Low sensitivity to acidification for the region and both water supplies.

MONTREAL

Water Supply	Fleuve Saint-Laurent	

Regional Data

Bedrock	calcareous clastic rocks and carbonate rocks interbedded or interspersed with non-calcareous sedimentary igneous and metamorphic rocks	intermediate-high buffering capacity
Surficial Deposits	likely to be calcareous	high buffering capacity
Precipitation pH	4.2 - 4.3	acidic

Raw Water Supply Data

1980

	Avg.[1]	Max.[1]	Min.[1]	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	-	135	116	less than 15
Alkalinity ($CaCO_3$, mg/L)	-	92	76	less than 15
Specific conductance (µmhos/cm)	310	330	280	less than 40
pH	7.9	8.0	-	less than 6.3

Conclusion

Low sensitivity to acidification for both the region and the water supply.

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[1] From monthly records.

OTTAWA CITY

Water Supply	Ottawa River	

Regional Data

Bedrock	limestone, dolomite and metamorphic equivalents	high buffering capacity
Surficial Deposits	likely to be calcareous	high buffering capacity
Precipitation pH	4.2 - 4.3	acidic

Raw Water Supply Data

June-July 1981

	Avg.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	N.A.	less than 15
Alkalinity ($CaCO_3$, mg/L)	15	less than 15
Specific conductance (µmhos/cm)	56	less than 40
pH	7.0	less than 6.3

Conclusion

The region in which this water supply is located shows a low sensitivity to acidification. The water supply itself could be classified as non-sensitive to acidification although the average value for alkalinity is at the limit.

OSHAWA CITY

Water Supply	Lake Ontario

Regional Data

Bedrock	calcareous clastic rocks and carbonate rocks interbedded or interspersed with non-calcareous sedimentary and metamorphic rocks	intermediate-high buffering capacity
Surficial Deposits	likely to be calcareous	high buffering capacity
Precipitation pH	4.1	acidic

Raw Water Supply Data

1977

	Range	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	139-149	less than 15
Alkalinity ($CaCO_3$, mg/L)	95-101	less than 15
Specific conductance (µmhos/cm)	N.A.	less than 40
pH	8.1-8.3	less than 6.3

Conclusion

Low sensitivity to acidification for both the region and the water supply.

METRO-TORONTO	Scarborough, Toronto, East York, North York, York, Etobicoke.	
Water Supply	Lake Ontario	
Regional Data		
Bedrock	calcareous clastic rocks and carbonate rocks interbedded or interspersed with non-calcareous	intermediate-high buffering capacity
Surficial Deposits	likely to be calcareous	high buffering capacity
Precipitation pH	4.1 - 4.2	acidic
Raw Water Supply Data	1980	

	Avg.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	137	less than 15
Alkalinity ($CaCO_3$, mg/L)	98	less than 15
Specific conductance (µmhos/cm)	N.A.	less than 15
pH	8.0	less than 6.3

Conclusion

Low sensitivity to acidification for both the region and the water supply.

MISSISSAUGA, BRAMPTON	(Region of Peel)	
Water Supply	Lake Ontario	
Regional Data		
Bedrock	calcareous clastic rocks and carbonate rocks interbedded or interspersed with non-calcareous sedimentary and metamorphic rocks	intermediate-high buffering capacity
Surficial Deposits	likely to be calcareous	high buffering capacity
Precipitation pH	4.1 - 4.2	
Raw Water Supply Data	1980	

	Range	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	138-147	less than 15
Alkalinity ($CaCO_3$, mg/L)	91-103	less than 15
Specific conductance (µmhos/cm)	N.A.	less than 40
pH	7.8-8.2	less than 6.3

Conclusion

Low sensitivity to acidification for both the region and the water supply.

BURLINGTON CITY

Water Supply	Lake Ontario	
Regional Data		
Bedrock	calcareous clastic rocks and carbonate rocks interbedded or interspersed with non-calcareous sedimentary and metamorphic rocks	intermediate-high buffering capacity
Surficial Deposits	likely to be calcareous	high buffering capacity
Precipitation pH	4.1 - 4.2	acidic
Raw Water Supply Data	1980	

	Range	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	129-140	less than 15
Alkalinity ($CaCO_3$, mg/L)	91-99	less than 15
Specific conductance (µmhos/cm)	N.A.	less than 40
pH	7.9-8.3	less than 6.3

Conclusion

Low sensitivity to acidification for both the region and the water supply.

HAMILTON CITY

Water Supply	Lake Ontario

Regional Data

Bedrock	calcareous clastic rocks and carbonate rocks interbedded or interspersed with non-calcareous sedimentary and metamorphic rocks	intermediate-high buffering capacity
Surficial Deposits	likely to be calcareous	high buffering capacity
Precipitation pH	4.1 - 4.2	acidic

Raw Water Supply Data

1980

	Avg.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	137	less than 15
Alkalinity ($CaCO_3$, mg/L)	97	less than 15
Specific conductance (µmhos/cm)	340-345	less than 40
pH	7.9	less than 6.3

Conclusion

Low sensitivity to acidification for both the region and the water supply.

ST. CATHARINES CITY

Water Supply	Welland Canal (Lake Erie)	

Regional Data

Bedrock	limestone, dolomite and metamorphic equivalents	high buffering capacity
Surficial Deposits	likely to be calcareous	high buffering capacity
Precipitation pH	4.1	acidic

Raw Water Supply Data

1980

	Avg.	Max.	Min.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	133	142	124	less than 15
Alkalinity ($CaCO_3$, mg/L)	98	102	94	less than 15
Specific conductance (µmhos/cm)	311			less than 40
pH	8.1	8.8	7.6	less than 6.3

Conclusion

Low sensitivity to acidification for both the region and the water supply.

KITCHENER CITY

Water Supply	groundwater

Kitchener's water supply is an aquifer situated in bedrock composed of carbonate-rich, siliceous sedimentary rock and dolomite. This groundwater is, therefore, very well buffered and has a pH generally in the range of 7.8-8.2. Further analysis of the susceptibility of this water supply is unnecessary since it is highly protected from acidification. The municipality is at present considering a surface water (Great Lakes) source.

WINDSOR CITY

Water Supply	Detroit River

Regional Data

Bedrock	limestone, dolomite and metamorphic equivalents	high buffering capacity
Surficial Deposits	likely to be calcareous	high buffering capacity
Precipitation pH	4.3 - 4.4	acidic

Raw Water Supply Data

1979

	Avg.	Max.	Min.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	105	113	102	less than 15
Alkalinity ($CaCO_3$, mg/L)	87	91	81	less than 15
Specific conductance (μmhos/cm)		(N.A.)		less than 40
pH	8.1	8.2	8.0	less than 6.3

Comment

Low sensitivity to acidification for both the region and the water supply.

LONDON CITY

Water Supply	Lake Huron (Grand Bend)

Regional Data

Bedrock	limestone, dolomite and metamorphic equivalents	high buffering capacity
Surficial Deposits	likely to be calcareous	high buffering capacity
Precipitation pH	4.3 - 4.4	acidic

Raw Water Supply Data

Oct. 13, 1981[1]

		Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	102	less than 15
Alkalinity ($CaCO_3$, mg/L)	85.7	less than 15
Specific conductance (µmhos/cm)	217	less than 40
pH	8.15	less than 6.3

Conclusion

Low sensitivity to acidification for both the region and the water supply.

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[1] Very stable values throughout the year.

THUNDER BAY CITY

Water Supplies	a) Loch Lomond b) Lake Superior

Regional Data

Bedrock	granite, granite gneiss, ortho-quartzite syenite	low buffering capacity
Surficial Deposits	areas of calcareous drift, transported from major carbonate outcrops	interdeterminate-intermediate buffering capacity
Precipitation pH	4.6 - 5.0	acidic

Raw Water Supply Data

October 1981

a) Loch Lomond

	Avg.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	26	less than 15
Alkalinity ($CaCO_3$, mg/L)	18	less than 15
Specific conductance (μmhos/cm)	58	less than 40
pH	7.1	less than 6.3

b) Lake Superior

	Avg.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$ mg/L)	45	less than 15
Alkalinity ($CaCO_3$ mg/L)	42	less than 15
Specific conductance (μmhos/cm)	105	less than 40
pH	7.7	less than 6.3

Conclusion

These water supplies are located in an area broadly classified as moderately sensitive to acidification. The water supplies themselves could be classified as non-sensitive to acidification although values for some of the parameters for Loch Lomond are close to the limit for sensitivity classification.

WINNIPEG CITY (also see Section 3.1)

Water Supply	Shoal Lake (Lake of the Woods)	

Regional Data

Bedrock	fractured igneous and metamorphic rock	low buffering capacity
Surficial Deposits	some thin, permeable tills and deposits of sands, varved clays and silts, containing some calcareous components	intermediate capacity
Precipitation pH	4.6 - 5.0	acidic

Raw Water Supply Data 1974

	Avg.	Max.	Min.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	74	84	67	less than 15
Alkalinity ($CaCO_3$, mg/L)	72	81	62	less than 15
Specific conductance (µmhos/cm)	159	171	137	less than 40
pH	7.7	7.9	7.6	less than 6.3

Conclusion

Intermediate to high sensitivity to acidification for the region but low sensitivity for the water supply at present.

REGINA CITY

Water Supply	Buffalo Pound Lake	

Regional Data

Bedrock	carbonate and other sedimentary rocks (clayey schist etc.)	intermediate-high buffering capacity
Surficial Deposits	deep, moderately calcareous till and lacustrine clays	high buffering capacity
Precipitation pH	5.5 - 6.5	non-acidic

Raw Water Supply Data

1980

	Max.	Min.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	245	155	less than 15
Alkalinity ($CaCO_3$, mg/L)	225	145	less than 15
Specific conductance (µmhos/cm)	750	500	less than 40
pH	8.5	7.8	less than 6.3

Conclusion

Low sensitivity to acidification for both the region and the water supply.

SASKATOON CITY (also see Section 3.3)

Water Supply	South Saskatchewan River	
Regional Data		
Bedrock	flat-lying sedimentary rocks	high buffering capacity
Surficial Deposits	calcareous tills over most of watershed	high buffering capacity
Precipitation pH	5.5 - 6.5	non-acidic

Raw Water Supply Data for 1968-1975

	Avg.	Max.	Min.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	170	195	121	less than 15
Alkalinity ($CaCO_3$, mg/L)	141	165	115	less than 15
Specific conductance (µmhos/cm)	397	494	304	less than 40
pH	-	8.7	7.4	less than 6.3

Conclusion

Low sensitivity to acidification for both the region and the water supply.

CALGARY CITY

Water Supplies	a) Elbow River, Glenmore Dam b) Bow River, Bearspaw Dam

Regional Data

Bedrock	sedimentary rocks (clayey schist, sandstone etc.)	intermediate-low buffering capacity
Surficial Deposits	slightly to moderately calcareous till over much of watershed	intermediate-high buffering capacity
Precipitation pH	5.5 - 6.0	non-acidic

Raw Water Supply Data

1980

a) Elbow River, Glenmore Dam

	Max.	Min.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	256	159	less than 15
Alkalinity ($CaCO_3$, mg/L)	181	109	less than 15
Specific conductance (µmhos/cm)	424	288	less than 40
pH	8.4	8.0	less than 6.3

b) Bow River, Bearspaw Dam

	Max.	Min.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$ mg/L)	182	124	less than 15
Alkalinity ($CaCO_3$ mg/L)	136	101	less than 15
Specific conductance (µmhos/cm)	323	218	less than 40
pH	8.5	8.23	less than 6.3

Conclusion

Intermediate sensitivity to acidification for the region but low sensitivity to acidification for the water supplies.

EDMONTON CITY

Water Supply	North Saskatchewan River

Regional Data

Bedrock	sedimentary rocks (clayey schist, sandstones, etc.)	intermediate-low buffering capacity
Surficial Deposits	slightly to moderately calcareous till over much of watershed	intermediate-high buffering capacity
Precipitation pH	5.5 - 6.0	non-acidic

Raw Water Supply Data

1980

	Avg.	Max.	Min.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	159	208	120	less than 15
Alkalinity ($CaCO_3$, mg/L)	134	170	102	less than 15
Specific conductance (µmhos/cm)	-	298	238	less than 40
pH	8.1	8.7	7.8	less than 6.3

Conclusion

Intermediate sensitivity to acidification for the region but low sensitivity to acidification for the water supply.

GREATER VANCOUVER (Surrey District, Vancouver City, and Burnaby District)

Water Supplies	a) Capilano Lake b) Seymour Lake c) Coquitlam Lake

Regional Data

Bedrock	meta-sedimentary rocks (gneiss and crystalline schist), may include volcanic rocks and granitic material	low buffering capacity
Surficial Deposits	very little calcareous component	low buffering capacity
Precipitation pH	5.0	acidic

Raw Water Supply Data 1980

a) Capilano Lake

	Avg	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	4.1	less than 15
Alkalinity ($CaCO_3$, mg/L)	2.4	less than 15
Specific conductance (µmhos/cm)	12	less than 40
pH	6.3	less than 6.3

b) Seymour Lake

	Avg.	Min.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	4.8	-	less than 15
Alkalinity ($CaCO_3$, mg/L)	2.9	-	less than 15
Specific conductance (µmhos/cm)	16	-	less than 40
pH	6.3	5.9	less than 6.3

c) Coquitlam Lake

Water hardness ($CaCO_3$, mg/L)	3.4	-	less than 15
Alkalinity ($CaCO_3$, mg/L)	1.6	-	less than 15
Specific conductance (µmhos/cm)	11	-	less than 40
pH	6.2	5.8	less than 6.3

Conclusion

High sensitivity to acidification for the region and the three water supplies.

3.5 Sensitivity of Water Supplies to Acidification and Subsequent Trace Metal Contamination for Selected Canadian Municipalities

The purpose of this section is to identify a number of Canadian communities that could potentially encounter an increase in toxic element concentrations in their water supplies due to acidic precipitation.

The first step in this exercise was to identify communities within areas of acidic precipitation that are located near significant natural or industrial sources of trace metals. This was mostly done using two maps from the Geological Survey of Canada (#1252A and 900A) which show the principal mineral areas in Canada. For some areas, available geochemical data helped in identifying probable communities of concern (Tremblay et Choinière 1978; B.E.S.T. 1979; Coker and Shilts 1979).

The second step in this process involved the identification of those communities having surface drinking water supplies. This information was found in the FACE (1975) report.

The third step consisted of gathering information on the nature and susceptibility to acidification of bedrock and surficial deposits. Most of this information is provided in Figures 3.1 and 3.2. Information on bed-rock surficial geology near Squamish, B.C. were taken from the Geological Survey of Canada (map #1250A) and from Clayton et al. (1977). Communities located in areas showing low buffering capacity were considered of immediate interest.

The last step consisted of gathering data on the raw water supply of these communities. Water hardness, alkalinity, specific conductance and pH were the parameters considered. By comparing the values obtained for each of the chosen communities with the limits for sensitivity classification, it was possible to determine if the water supply itself was sensitive to acidification.

The municipalities concerned were contacted to obtain values of the considered parameters. When possible, values (average. maximum and minimum) were obtained for 1980. However, in some cases, it was only possible to obtain an average value for each parameter for 1980 while in other cases, even fewer data were available.

In this section, all available data for 10 communities are presented with a short comment on each. For Rouyn, Quebec, considerable relevant data were available. Data for the other communities, especially concerning the occurrence of toxic elements, related to the region rather than specifically to the water supply.

Rouyn is the only community considered herein having a water supply that is clearly susceptible to trace metal contamination due to acidification. More extensive limnological data are required before definite conclusions on metal toxicity hazards can be made for other municipal water supplies.

SQUAMISH, BRITISH COLUMBIA

Water Supply	Stawamus River	

Regional Data

Bedrock	granite and associated plutonic rocks	low buffering capacity
Surficial Deposits	soils mainly sandy and stoney, acidic and non-calcareous	low buffering capacity
Precipitation pH	5.0	acidic
Potential toxic elements	arsenic (As) lead (Pb) zinc (Zn), cadmium (Cd)	
Mined ore	gold (Au), silver (Ag), lead (Pb), zinc (Zn) and cadmium (Cd)	

Raw Water Supply Data

November 1980 - November 1981

	Avg.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	11.5	less than 15
Alkalinity ($CaCO_3$, mg/L)	N.A.	less than 15
Specific conductance (µmhos/cm)	N.A.	less than 40
pH	7.1	less than 6.3

		Max. acceptable Concentration[1]	Drinking Water Obj.[1]
Lead (µg/L)	1	50	≤ 1
Arsenic (µg/L)	31	50	≤ 5

---

1. from Health and Welfare Canada (1978)

SQUAMISH

Comment

The regional data show that the bedrock has a low buffering capacity and hence would be sensitive to the acidic precipitation (pH 5.0) the region receives. There is a possibility that heavy metals contained in bedrock, surficial deposits and in tailings areas, may be released to surficial waters due to acidification. Health and Welfare (1978) drinking water objectives for arsenic are not met by this water supply, although maximum acceptable concentrations are generally not exceeded. Because of the low buffering capacity of the bedrock in the area, acidification is a possible long-term perspective.

WAWA, ONTARIO

Water Supply	Wawa Lake

Regional Data

Bedrock	volcanic and sedimentary rocks and their metamorphic equivalents	intermediate - low buffering capacity
Surficial Deposits	high probability of occurrence of calcareous. fine grained sediments	indeterminate or intermediate buffering capacity
Precipitation pH	4.4 - 4.6	acidic
Potential toxic elements	arsenic (As)	
Mined ore	iron (Fe)	

Raw Water Supply Data

1980

	Avg.	Max.	Min.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	75	80	56	less than 15
Alkalinity ($CaCO_3$, mg/L)	42	47	27	less than 15
Specific conductance (µmhos/cm)	167	184	162	less than 40
pH	7.5	8.1	6.7	less than 6.3

Comment

The data related to the Wawa region indicate an intermediate to high sensitivity to acidification. Coker and Shilts (1979) report that the lake sediments contain a high quantity of arsenic. This arsenic could be released to the water if acidification occurs in Wawa Lake.

Although raw water supply data do not indicate sensitivity of Wawa Lake to acidification, this could become a problem in the future if alkalinity levels decline due to acid inputs

SAULT STE. MARIE, ONTARIO

Water Supply	St. Mary's River

Regional Data

Bedrock	limestone, dolomite and metamorphic equivalents	high buffering capacity
Surficial Deposits	high probability of occurrence of calcareous, fine grained sediments	indeterminate or intermediate buffering capacity
Precipitation pH	4.4 - 4.6	acidic
Potential toxic elements	lead (Pb), zinc (Zn)	
Mined ores	lead (Pb), zinc (Zn), silver (Ag)	

Raw Water Supply Data

1980

	Avg.	Max.	Min.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	46	50	45	less than 15
Alkalinity ($CaCO_3$, mg/L)	45.5	50	43	less than 15
Specific conductance (μmhos/cm)	101	125	95	less than 40
pH	8.2	9.1	7.9	less than 6.3

Comment

The general area of Sault Ste. Marie shows an intermediate to high buffering capacity. However, since the area is a producer of lead, zinc and silver, it is probable that sediments of rivers and lakes contain some trace metals from bedrock, tailings and smelting. The source of the St. Mary's River is Lake Superior, a very large, well-buffered lake. It is unlikely that significant acidification will occur in the foreseeable future. Thus, it is unlikely that hazardous quantities of trace metals will be mobilized from the sediments of the St. Mary's River due to acidic precipitation.

BRACEBRIDGE, ONTARIO

Water Supply	Lake Muskoka	

Regional Data

Bedrock	granite, granite-gneiss, ortho-quartzite syenite	low buffering capacity
Surficial Deposits	high probability of occurrence of calcareous, fine grained sediments	indeterminate or intermediate buffering capacity
Precipitation pH	4.2 - 4.3	acidic

Raw Water Supply Data

March 1981, May 1980

	Avg. March 1981	Avg. May 1980	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	16	16	less than 15
Alkalinity ($CaCO_3$, mg/L)	3	5	less than 15
Specific conductance (µmhos/cm)	50	51	less than 40
pH	6.8	6.1	less than 6.3

Comment

The general area of Bracebridge shows an intermediate to high sensitivity to acidification. The water of Lake Muskoka, the drinking water supply, borders the limit for sensitivity classification and at times shows an average pH of less than 6.3. Bracebridge is located in an area where the calcite saturation index (CSI) is over 4 (Figure 2.10) which means that this area is susceptible to pH depression below 5 after acidification. Fortunately, this is not a mineral producing area and severe contamination by toxic trace elements is unlikely.

BANCROFT, ONTARIO

Water Supply	Lake Clarke	

Regional Data

Bedrock	granite, granite-gneiss, ortho-quartizite, syenite	low buffering capacity
Surficial Deposits	likely to be calcareous in some areas and non-calcareous in others	low to high buffering capacity
Precipitation pH	4.1 - 4.2	acidic
Potential toxic elements	lead (Pb), molybdenum (Mo)	
Mined ores	uranium (U), iron (Fe)	

Raw Water Supply Data

1978-1980

	Avg.	Max.	Min.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	41	65	33	less than 15
Alkalinity ($CaCO_3$, mg/L)	29	37	25	less than 15
Specific conductance (μmhos/cm)	85	110	78	less than 40
pH	7.2	8.6	6.7	less than 6.3

Comment

The precipitation in this area is very acidic (pH 4.1-4.2) and it is fortunate that some surficial deposits show a high buffering capacity. The bedrock in the overall area shows a low buffering capacity. Uranium and iron mines are found in the area, and other important minerals present include lead and molybdenum. As Lake Clarke shows no sensitivity to acidification at present, it is unlikely that any toxic elements will present a health hazard in the near future.

MARMORA, ONTARIO

Water Supply	Crowe River

Regional Data

Bedrock	calcareous, clastic rocks and carbonate rocks interbedded or interspersed with non-calcareous sedimentary, igneous and metamorphic rocks	intermediate - high buffering capacity
Surficial Deposits	likely to be calcareous	high buffering capacity
Precipitation pH	4.1 - 4.2	acidic
Potential toxic elements	arsenic (As), zinc (Zn), nickel (Ni), copper (Cu), cobalt (Co), lead (Pb) (in neighbouring Moira River)[1]	
Mined ores	sulphur (S)	

Raw Water Supply Data

1980

	Avg.	Max.	Min.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	80	96	65	less than 15
Alkalinity ($CaCO_3$, mg/L)	69	73	58	less than 15
Specific conductance (µmhos/cm)	167	185	145	less than 40
pH	7.7	7.8	7.6	less than 6.3

Comment

Precipitation in this area is very acidic (pH 4.1-4.2), however, the bedrock and the surficial deposits show intermediate to high buffering capacity and the Crowe River shows also no sensitivity to acidification. This water supply seems, therefore, to be well protected from acidification at present.

---

[1] From Mudroch and Capobianco (1979).

MARMORA, ONTARIO

Sulphur mines are present in the area and several toxic elements (notably As) occur in high concentrations in the neighbouring Moira River watershed (Mudroch and Capobianco 1979). Some of these elements may also occur to some extent in the water supply of Marmora.

Although the Crowe River is apparently safe from the effects of acidification in the foreseeable future, an investigation of trace element contamination in the watershed may be warranted.

ROUYN-NORANDA, QUEBEC

Water Supply Lac Duffault

Regional Data

Bedrock	volcanic and sedimentary rocks and their metamorphic equivalents	intermediate - low buffering capacity
Surficial Deposits	calcareous drift. glacially transported from major carbonate outcrops	indeterminate or intermediate buffering capacity
Precipitation pH	4.3 - 4.4	acidic
Potential toxic elements	zinc (Zn), arsenic (As), mercury (Hg), copper (Cu), cadmium (Cd), lead (Pb) (in Lac Duffault sediments)[1]	
Mined ores	gold (Au), copper (Cu), zinc (Zn), silver (Ag)	

Raw Water Supply Data

	Range	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)[b]	75 - 78	less than 15
Alkalinity ($CaCO_3$, mg/L)[a]	15 - 21	less than 15
Specific conductance (μmhos/cm)[b]	162	less than 40
pH[a]	4.1	less than 6.3

---

[1] From B.E.S.T. 1979

[a] February 1978
[b] June 1978

ROUYN-NORANDA, QUEBEC

The physico-chemical data for Lac Duffault are very comprehensive. In addition to the parameters presented earlier, the B.E.S.T. (1979) report gives the following data:

Concentrations of trace metals in Lac Duffault water (µg/L)		Max. acceptable concentration[1]	Drinking water objective[1]
Arsenic (As)	<2.0 - 5.0	50	5
Cadmium (Cd)	3.2 - 7.7	5	≤1
Copper (Cu)	14 - 51.4	1 000	<1 000
Mercury (Hg)	0.06 - 0.28	1	≤0.2
Lead (Pb)	0.2 - 28.9	50	≤1
Zinc (Zn)	310 - 440	5 000	5 000

Concentrations of trace metals in Lac Duffault sediments (mg/kg)		Definition of Concentration Level (mg/kg)[2]	
Copper (Cu)	1 178	extremely contaminated	>500
Zinc (Zn)	2 193	extremely contaminated	>1 000
Arsenic (As)	42	very contaminated	25-50
Mercury (Hg)	0.202	extremely contaminated	> 0.2
Cadmium (Cd)	17	extremely contaminated	>12
Lead (Pb)	375	extremely contaminated	>200

Comment

The municipal water quality data provided for Rouyn may be somewhat inaccurate. By definition, total alkalinity is determined by titration with acid to pH 4.5 and no alkalinity remains in water at a lower pH (American Public Health Association 1975). Thus, the reported pH of 4.1 for the Rouyn water supply is too low for the alkalinities reported. Nonetheless, it is quite obvious that the water supply is extremely acidic.

---

1. From Health and Welfare Canada (1978)
2. From B.E.S.T. (1979)

ROUYN-NORANDA, QUEBEC

The regional geology (bedrock and surficial) near Rouyn offers only low to intermediate buffering capacity. Precipitation in the area has an average pH of 4.3-4.4 according to Figure 2.1; however, local precipitation may be even more acidic due to smelting operations at Noranda. Acid may also be generated by tailings areas, thereby contributing to the local problem.

Heavy metal contamination in Lac Duffault can be attributed primarily to important tailings areas located along two tributaries, the Duprat River and Vauze Creek, although atmospheric pollution also contributes to metal contamination (B.E.S.T. 1979).

Concentrations of cadmium in the water supply exceed the Health and Welfare Canada (1978) maximum acceptable concentration of 5 µg/L. Levels of arsenic, mercury and lead approach or exceed drinking water objectives. These observations indicate that the quality of the water supply for Rouyn is questionable. A rigorous monitoring program should be instituted to provide an "early warning system" for contamination hazards. Measures should be undertaken to control metal contamination and acidification at the regional level since threats to human health will increase with continuing contaminant releases. The adequacy of the municipal water treatment system for removal of metals should be carefully reviewed. Also, the potential for mobilization of contaminants (metals, asbestos) from within the water distribution system should also be assessed. Ultimately, it may be necessary to find an alternate municipal water source.

MATANE, QUEBEC

Water Supply	Rivière Matane

Regional Data

Bedrock	volcanic and sedimentary rocks and their metamorphic equivalents	intermediate - low buffering capacity
Surficial Deposits	likely to have calcareous deposits	intermediate buffering capacity
Precipitation pH	4.4 - 4.6	acidic
Potential toxic elements[1]	copper (Cu), zinc (Zn), nickel (Ni), manganese (Mn) (in sediments of the river's tributaries)	
Mined ores[2]	(the nearest mine is in Murdochville, copper (Cu), molybdenum (Mo), silver (Ag), selenium (Se), tellurium (Te), bismuth (Bi); this mining operation is not in the Rivière Matane watershed)	

Raw Water Supply Data

1979

	Avg.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	214	less than 15
Alkalinity ($CaCO_3$, mg/L)[a]	188	less than 15
Specific conductance (µmhos/cm)	N.A.	less than 40
pH	7.55	less than 6.3

---

1. From Tremblay and Choinière (1978).
2. From GSC (1979).

MATANE, QUEBEC

Additional data are available on concentrations of trace metals in Matane River sediments (from Tremblay and Choinière 1978):

	Copper in sediments (mg/kg)	Definition of Contamination Level[1] (mg/kg)
Copper	173 - 345	contaminated (100-200) to very contaminated (200-500)
Zinc	493 - 2 640	very·contaminated (500-1000) to extremely contaminated (>1 000)
Nickel	70 - 140	-
Manganese	3 801 - 7 600	-

Comment

Although the regional bedrock has only an intermediate to low buffering capacity, the surficial deposits appear to offer some degree of buffering protection and as a result, Rivière Matane is very resistant to acidification at Matane.

High levels of trace metals in Rivière Matane sediments indicate a potential source of contamination of the municipal water supply. These metals do not appear to have a major regional anthropogenic source and are primarily due to geologic sources in all likelihood. Fortunately, the neutral pH and high alkalinity indicate that trace metals should remain in the particulate phase in Rivière Matane. Acidification may lead to the depletion of buffering capacity in the long-term, potentially causing a contamination problem.

---

[1] From B.E.S.T. (1979).

BAIE VERTE, NEWFOUNDLAND

Water Supplies
a) Rattling Brook
b) Baie Verte Brook

Regional Data

Bedrock	Downstream areas - volcanic and sedimentary rocks and their metamorphic equivalents	intermediate - low buffering capacity
	Upstream areas - granite, granite-gneiss, orthoquartzite, syenite	low buffering capacity
Surficial Deposits	likely to non-calcareous	low buffering capacity
Precipitation pH	>4.6	likely to be acidic
Potential toxic elements	copper (Cu)	
Mined ores	copper (Cu), gold (Au), silver (Ag)	

Raw Water Supply Data

July 1979

a) Rattling Brook

	Avg.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	14.01	less than 15
Alkalinity ($CaCO_3$, mg/L)	6.4	less than 15
Specific conductance (µmhos/cm)	47.92	less than 40
pH	6.25	less than 6.3

BAIE VERTE, NEWFOUNDLAND

b) Baie Verte Brook

	Avg.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	18.58	less than 15
Alkalinity ($CaCO_3$, mg/L)	13.0	less than 15
Specific conductance (µmhos/cm)	53.53	less than 40
pH	6.97	less than 6.3

Comment

The regional geologic data show that this area has a low to intermediate buffering capacity. Of the two water supplies, Rattling Brook is very sensitive to acidification in terms of alkalinity, hardness and pH. Baie Verte Brook borders on being sensitive and by definition, is sensitive in terms of alkalinity.

Although data on metal contamination in the Baie Verte area were not available, the presence of a copper-gold-silver mining operation indicates that some metal contamination in regional watersheds is likely. Further investigation of water and sediment quality in Rattling Brook and Baie Verte Brook is warranted, particularly in light of the sensitivity of the region to acidification.

BATHURST, NEW BRUNSWICK

Water Supplies
a) Carter's Brook
b) Middle River

Regional Data

Bedrock	volcanic and sedimentary rocks and their metamorphic equivalents	intermediate - low buffering capacity
Surficial Deposits	Downstream areas - high probability of occurrence of calcareous, fine-grained marine sediments	indeterminate or intermediate buffering capacity
	Upstream areas - likely to be non-calcareous	low buffering capacity
Precipitation pH	4.4 - 4.6	acidic
Potential toxic elements	lead (Pb), zinc (Zn), copper (Cu)	
Mined ores	zinc (Zn), lead (Pb), copper (Cu), silver (Ag), bismuth (Bi), gold (Au)	

Raw Water Supply Data

November 1981

a) Carter's Brook

	Avg.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	90	less than 15
Alkalinity ($CaCO_3$, mg/L)	N.A.	less than 15
Specific conductance (µmhos/cm)	N.A.	less than 40
pH	7.2	less than 6.3

BATHURST, NEW BRUNSWICK

b) Middle River

	Avg.	Limit for Sensitivity Classification
Water hardness ($CaCO_3$, mg/L)	20	less than 15
Alkalinity ($CaCO_3$, mg/L)	N.A.	less than 15
Specific conductance (μmhos/cm)	N.A.	less than 40
pH	6.6	less than 6.3

Comment

From the regional data available, Bathurst's water supplies lie in an area sharing an intermediate to high sensitivity to acidification. On the other hand, data on the water supplies themselves indicate no sensitivity to acidification at present.

Many metal mines occur in the Bathurst area, producing zinc (Zn), copper (Cu), silver (Ag), bismuth (Bi) and gold (Au). It is possible that acidic precipitation causes metals to be leached from the bedrock and to be transported to regional surface waters. Tailings areas are also probable sources of metal contamination in regional waters. Unfortunately, data on trace metal contamination in the Bathurst area were unavailable.

4. DATA SOURCES

4.1 Data Sources of Precipitation Chemistry in Canada

The increasing acidity (decreasing pH) of precipitation over time in North America can be traced back at least to the 1950s and '60s by deriving pH from a balance of chemical constituents in the precipitation (Cogbill 1976; Likens et al. 1979). The results, plotted on contour maps and connecting points at considerable distance showing similar acidity, have several weaknesses. For example, precipitation pH can vary substantially over short distances. In one case, the average precipitation pH falling on the Canadian Shield in the Haliburton-Muskoka area was observed to be more than one pH unit lower than that observed simultaneously several miles away, but off the Shield (Dillon et al. 1978). Localized differences may be due to atmospheric dust loadings or meteorological effects.

The federal government is currently operating two extensive measurement programs which monitor precipitation chemistry data. CANSAP (Canadian Network for Sampling Precipitation) operates 53 sampling sites throughout Canada (listed in Table 4.1). Each sample is analyzed for acidity and soluble major ions including sulphate and nitrate. This program has been under way since January 1977.

The APN (Canadian Air and Precipitation Monitoring Network) has been in operation since the end of 1978 and monitors wet and dry deposition chemistry. This network includes five selected locations in eastern Canada, with more stations to be added this year (1981).

Provincially, the east has a small, intense network of pH monitoring facilities in Nova Scotia (in operation since 1977). Numerous studies have been undertaken by the Ministry of the Environment in Ontario since 1976 for the Sudbury and Muskoka-Haliburton and Great Lakes regions, including wet and dry deposition studies, and lake pHs. Specific details are given in Figure 4.1. Ontario Hydro has operated rain collectors at nine sites (located near their generating stations) since 1974. Manitoba monitors SO_2 levels in a region surrounding their two smelters in Flin Flon and Thompson, with records dating from 1974. Snowpack chemistry monitoring was also initiated in the boreal forest in 1980.

Table 4.1: Stations in Atmospheric Chemistry Networks

Program	Region Covering			Time
A P N (Canadian Air and Precipitation Monitoring Network)	5 sites	Parameters monitored		Starting
	1. Kenora	Precipitation,	Air	15 Nov. 1978
	2. Chalk River	Precipitation,	Air	1 Nov. 1978
	3. Long Point	Precipitation,	Air	Jan. 1979
	4. Kejimkujik Park	Precipitation,	Air	May 1979
	5. CN Tower	-	Air	June 1977
	Precip. analysed for pH, $SO_4^=$, NO_3^-, Cl^-, Ca^{++}, NH_4^+, Mg^{++}, Na^+, K^+, and total phosphorus, particulates, SO_2.			
CANSAP (Canadian Network for Sampling Precipitation)	B.C. Terrace Port Hardy Vancouver Kelowna Revelstoke Pr. George Ft. St. John Ft. Nelson Yukon Whitehorse N.W.T. Inuvik Ft. Reliance Hay River Alberta Edson Rocky Mountain House Coronation Lethbridge Ft. McMurray	Sask. Cree Lake Kindersley Wynyard Manitoba Le Pas Dauphin Bisset Churchill Ontario Trout Lake Pickle Lake Ela Atikokan Moosonee Kapuskasing Dorset Kingston Peterborough Mt. Forest Simcoe Harrow	Quebec St. Hubert Maniwaki Quebec City Chibougamau Sept-Îles Nitchoquon Fort Chimo Nfld. Goose Bay Gander Stephenville N.B. Charlo Acadia Fes Saint-Jean N.S. Truro Kejimkujik Shelburne Sable Island	Jan. 1977 to present
	Collects precipitation chemistry data $SO_4^=$, NO_3^-, Cl^-, NH_4^+, K^+, Mg^{++}, Ca^{++}.			

Modelling SO_2 deposition rates from point source emissions comprises the main bulk of data from the Prairies. British Columbia data are collected along the coast of B.C. by the provincial government.

New Brunswick, Newfoundland, Quebec and Saskatchewan are establishing networks in 1981.

4.2 Geochemical Data Sources

The buffering capacity of a watershed is related largely to the bedrock and surficial geochemistries. These may range from calcareous basins with a large capacity for buffering, to granite basins with an insignificant capacity for buffering. Bedrock and surficial rock types and their potential buffering capacities may be interpreted from geological maps published by provincial Departments of Mines (or equivalent) or by the Geological Survey of Canada (GSC). These maps identify predominant rock types on a regional basis and, therefore, buffering potential and areal distribution within that region.

Geological information contained within the geochemical files of the Geological Survey of Canada has recently been compiled, interpreted, and summarized to produce maps describing terrain sensitivity to acidic precipitation. The results, similar to those in Figures 3.1 and 3.2, have been reproduced in three maps covering eastern Canada from the Manitoba border to the Maritimes, the part of the country of greatest concern. They will be available shortly from agents handling federal government publications.

The potential contribution of surficial materials to buffering capacities and terrain sensitivities has not been incorporated into the GSC summary maps. Surficial material types and their approximate depth of cover may be obtained from land inventory or classification maps published by provincial Department of Natural Resources (or equivalent). From these, areal estimates can be made of their relative contribution to regional buffering capacities within the watershed.

4.3 Water Quality Data Sources

In determining the total buffering capacity of a water supply, the parameters of greatest interest (as indicated in the discussion in Section 2.3.2, Lake Water Chemistry) are pH, specific conductance, calcium carbonate alkalinity, and total alkalinity. Several of these parameters constitute parts of regular monitoring programs of watersheds conducted by provincial Departments of Environment (or equivalent). Data may be found in provincial or federal water quality summaries (for example, Ontario Ministry of Environment 1980; Canada, Fisheries and Environment Canada 1977; NAQUADAT). In addition, many municipalities produce an annual water quality report (raw water), summarizing basic water quality parameters such as those relating to pH and buffering capacity. Although long-term trend data may not be readily available, the current relative sensitivities of water supplies may be determined by interpretation of these parameters.

4.3.1 Trace Elements - Water and Sediment Chemistry

Water and sediment are generally considered to be good environmental composites of geochemical conditions within the drainage area. Their chemical quality has been evaluated in relation to the physical environment (Reeder et al. 1972), and for exploration purposes. Geochemical surveys of water and sediment quality have been conducted by the GSC in 34 areas in Canada and 10 detailed areas, with a differing range of parameters determined in the areas. The emphasis has been upon geochemical exploration and elements of economic interest. These data have been recently summarized in map form by the GSC for publication, and are available from agents handling federal government publications.

This information is of interest insofar as it provides an indication of local and regional element distribution patterns in the area of study. It should be cautioned, however, that geologists are more frequently interested in absolute abundance of elements and, therefore, normally use complete extraction with substances such as hydrofluoric acid. The results are, therefore, not usually indicative of mineralogic form or mobility of the element and may overestimate amounts available for mobilization.

Trace element concentrations of water supplies have not been further considered in this report, because they constitute an aspect of a detailed study which should be conducted after a preliminary identification of sensitive water supplies is complete.

4.4 A Few Limitations to Use of Data Sources

It is often possible to conduct preliminary analyses of the susceptibility of public water supplies to acidic precipitation using available data and mapping. Such mapping would include bedrock mapping, (e.g., Shilts 1981), surficial till mapping, geochemical exploration mapping, and chemical precipitation mapping. The approaches outlined in Section 3 involve maps such as the pH of precipitation (Figure 2.1) and bedrock mapping (Figure 2.4) on a coarse scale for North America and maps of finer detail for specific watersheds. However, comparisons of bedrock mapping (e.g., Figure 2.4) with observed surface water chemistry are needed before conclusions concerning the validity of bedrock mapping as a method for assessing susceptibility of lake waters can be validated.

Throughout most areas of Canada, the bedrock is overlain by glacial deposits which vary considerably in their thickness, permeability and mineralogy. In most cases, it is the buffering capacity of these glacial deposits which will be responsible for controlling the acidity of surface waters in a watershed. These glacial deposits are in turn derived from "up ice" of their present positions and accordingly, it may be possible to have a watershed which has a very low sensitivity to acidification located upon bedrock which has very low buffering capacity. To a lesser degree, the reverse may also hold true. Since very little information is available on the mineralogy, depth and permeability of the glacial deposits covering acid sensitive bedrock areas (as defined by Shilts 1981), educated guesses are often necessary when interpreting such data. In the absence of such data, it may be necessary to work backwards from the present, integrated watershed chemistry and precipitation history.

Just as it is necessary to understand the nature of the surficial deposits with respect to their "neutralization" or "buffering capacity" it is also necessary to evaluate their potential for supplying potentially deleterious trace elements to drinking water. This potential relates both to anthropogenic and natural sources. While a relatively good body of data exists relating to anthropogenic sources, natural sources are quite often the major potential contributors of trace elements to water supply. These natural sources can be either components of surficial deposits or of bedrock.

While acidification of public waters poses some problems for municipal water supply systems (e.g., pipe corrosion), the possible mobilization of heavy metals and other contaminants in the drainage basin by relatively acidic waters is of significant concern to managers of water supply systems. It is to this latter question that this section particularly addresses itself.

Elevated concentrations of trace metals in the sediments of certain lakes influenced by acidic precipitation may or may not reflect mobilization of these metals by acidification. Seemingly elevated concentrations may result from atmospheric inputs rather than from weathering of the watershed or may be in a mineral form which is not particularly susceptible to attack by low concentrations of strong acids. Knowledge of both atmospheric inputs and forms of weathered particles is essential in the assessment of the susceptibility of public water supplies. This is analogous to the classical sanitary survey in which an inventory of actual discharges of pollutants upstream of a water supply is deemed just as essential as actual measurements of pollutant concentrations in the incoming water.

An example of the influence of atmospheric inputs upon lake water and sediment chemistry is provided by lakes in the Sudbury area of Ontario. Within 30-50 km of Sudbury, the pH of precipitation and of the adjoining lakes shows a marked increase outward from Sudbury, representing the influence of sulfur dioxide produced by the roasting of ores and resultant stack emissions from the smelters. Spot samples of lake sediments in neighbouring lakes show elevated concentrations of trace metals such as nickel. One might, as a first approximation suggest that mobilization of trace metals by acidic precipitation has occurred. However, present evidence seems irrefutably to reject this suggestion. The areal distribution of nickel in the bottom sediments of Sudbury area lakes and in atmospheric precipitation is shown in Figures 4.2(a) and 4.2(b). Similar trends of nickel concentrations in the lake waters are also observed (Sempkin 1975). The similarity of the elliptical patterns, the exponential decrease with distance from Sudbury and examination of other trace metals and sulfur dioxide caused Simpkin to conclude that atmospheric transport from the nickel smelting areas of Sudbury was the major source of these elevated concentrations. Sediments in Georgian Bay also appear to reflect atmospheric loading from the Sudbury area whereas nickel in the remainder of the Great Lakes reflects natural weathering processes (Snodgrass 1980).

Sempkin also observed that a larger fraction of the total metal in the water column of these lakes was soluble at lower pHs. Metals examined include nickel, iron, zinc and copper. Typical evidence of this relationship is given in Figure 4.2(c) for nickel. Since lake waters of low pH have higher metal concentrations, the potential problems for water supply management are amplified. The lack of particulate forms make metal removal difficult in conventional water filtration plants unless metal coagulants are capable of inducing their precipitation.

For assessing whether metal levels in lake sediments are potentially susceptible to mobilization, examination of their distribution vertically, of their distribution between particulate and soluble forms, of their mineral association, and of their acid leachability are often essential, but typically not available from normal data sources. Examination of the distribution of a metal from a sediment core (perhaps representing 100 years of history) allows one to decide whether significant changes have occurred in watershed processes or atmospheric inputs. The concentrations of nickel and other trace metals in lake sediments near Sudbury show marked decreases with sediment depth, reflecting the increased input from anthropogenic sources. Examination of the porewater concentrations of metals provides some evidence for the quantity which may be mobilized under acidic conditions for lake sediments which are more acidic than the overlying lake water due to microbial decomposition processes.

Whether a metal may be potentially mobilized also depends on its form upon entering the lake. If adsorbed to the surface of silts or clays, it is more easily leached under moderately low pH conditions than if it is coprecipitated onto a surface or if it is incorporated within a clay lattice or in a mineral matrix. Typically, total metal concentrations are measured in lake sediments; occasionally, a weak acid extraction is used. A weak acid extraction would simulate the potential short-term release of metals under acidifying conditions. Whether it is the best simulator of long-term conditions depends upon whether the sediment particles act as an ion exchanger (e.g., H^+ exchanging for a metal).

For certain metals, the inorganic form is relatively insoluble over typical pH ranges of acidic lakes while the organic form is relatively soluble. Examples are methyl forms of mercury and arsenic. Elemental mercury is quite insoluble in water. Such forms may be converted to methyl-mercury by anaerobic bacteria. These organic-metal forms can bioaccumulate in food chain and reach dangerous levels in fish. For water supply management, the general question of concern is whether there is any significant amount of methyl-mercury in a particulate organic form (e.g., in algae or zooplankton) and whether coagulation-filtration processes are capable of removing any of these particulates. To assess the potential development of such particulate forms of mercury, an analysis of the anaerobic community of the lake sediments is needed as well as an evaluation of the mobilization potential of any deposits bearing mercury in the watershed.

Finally a review of data, supplied by various agencies, to this study has revealed a series of internal inconsistencies. This would suggest that many of the analytical methods or equipment being used at the local level do not have sufficient accuracy to produce data with enough precision to enable definitive comments to be made about the sensitivity of the water supply. Where this is obvious in the data it has been noted. In other instances no level of accuracy can be estimated and it was assumed for this study that the data are reasonably accurate.

5. CONCLUSIONS AND RECOMMENDATIONS

The foregoing report describes fundamental factors to be considered in assessing potential buffering capacities on a watershed or regional basis. It also presents a simple method for estimating the sensitivity of a water supply to acidification, based upon readily available information. The method is preliminary and overview in nature, and is intended to provide a means by which priorities may be placed on water supplies for more detailed study. It should therefore be used with the recognition that individual and localized factors, such as significant groundwater input, may substantially alter the estimated sensitivity of a water supply.

It is recommended that this relatively simple, overview method of estimating the susceptibility of a water supply to acid precipitation effects be applied to numerous other water supplies in Canada. By using the available data to rank the water supplies in categories of relative sensitivities, and by recording data gaps, priorities can be determined for future study.

It is further recommended that several of the water supplies, estimated by the overview method to be most sensitive, be evaluated using the detailed methodologies outlined in Section 2.3 SURFACE WATER SYSTEMS. These would consider first the alkalinity, pH, and conductivity of the water supply; then, alkalinity titration curves would be determined from field sampling; and finally, the effects of the drainage basin (groundwater and surface water) and internal lake processes on the creation and consumption of alkalinity in the lake water would be considered. These detailed methods will enable estimates to be made of the rate of pH decrease in the sensitive water supplies.

This approach will provide the management tools required to develop an effective monitoring program. Monitoring can then be initiated at those water supplies determined to be most sensitive, and most at risk in the short term. Parameters for regular or continuous monitoring should be limited to pH, specific conductivity, and alkalinity. Trace element concentrations in the water supply can then be characterized by periodic sampling in conjunction with cycles in the pH, specific conductivity, or alkalinity - for example, during spring peak flow when acid inputs may be highest, and again during a low flow period.

In this way, with a relatively small scale study program, information will be collected which is useful in characterizing the water supply and how it is affected by acidic precipitation over time. The information will also be valuable in determining the suitability of water treatment methods in Canadian drinking water supply systems. It is a simple and cost-effective approach to a broad scope and complex problem.

In Sections 3.4 and 3.5 several major Canadian water supplies and smaller, more local supplies were evaluated. Of the water supplies to major cities those of both Halifax and to a somewhat lesser degree Vancouver are evaluated as potentially sensitive. Based upon the data in this report, we recommend that a more detailed review of the Halifax water supply be carried out. This would involve a confirmation of the data presented, a review of any historical data that may be available to determine any type of temporal trends, and an analysis of the raw and treated water supplies for trace elements that may be expected to be liberated within the watershed under acidic leaching conditions. Following an analysis of the water supply, we would recommend that a comparable analysis be carried out on the surficial oxidized layer and the reduced sedimentary layer in Pockwock Lake, the main water source. If potentially toxic elements are present in significant quantities, a study should be carried out to investigate the effects of acidification on the liberation of these elements and the effectiveness of the water treatment system in removing them prior to distribution.

Of the smaller centres investigated, Rouyn-Noranda, although not necessarily showing a response to acidic precipitation, would appear to warrant further detailed study. In this instance the data would appear to call for a routine monitoring of the raw and treated water supplies for potentially toxic trace elements and a study comparable to the one recommended for Halifax in which potential liberation of trace elements from Lac Duffault will be investigated.

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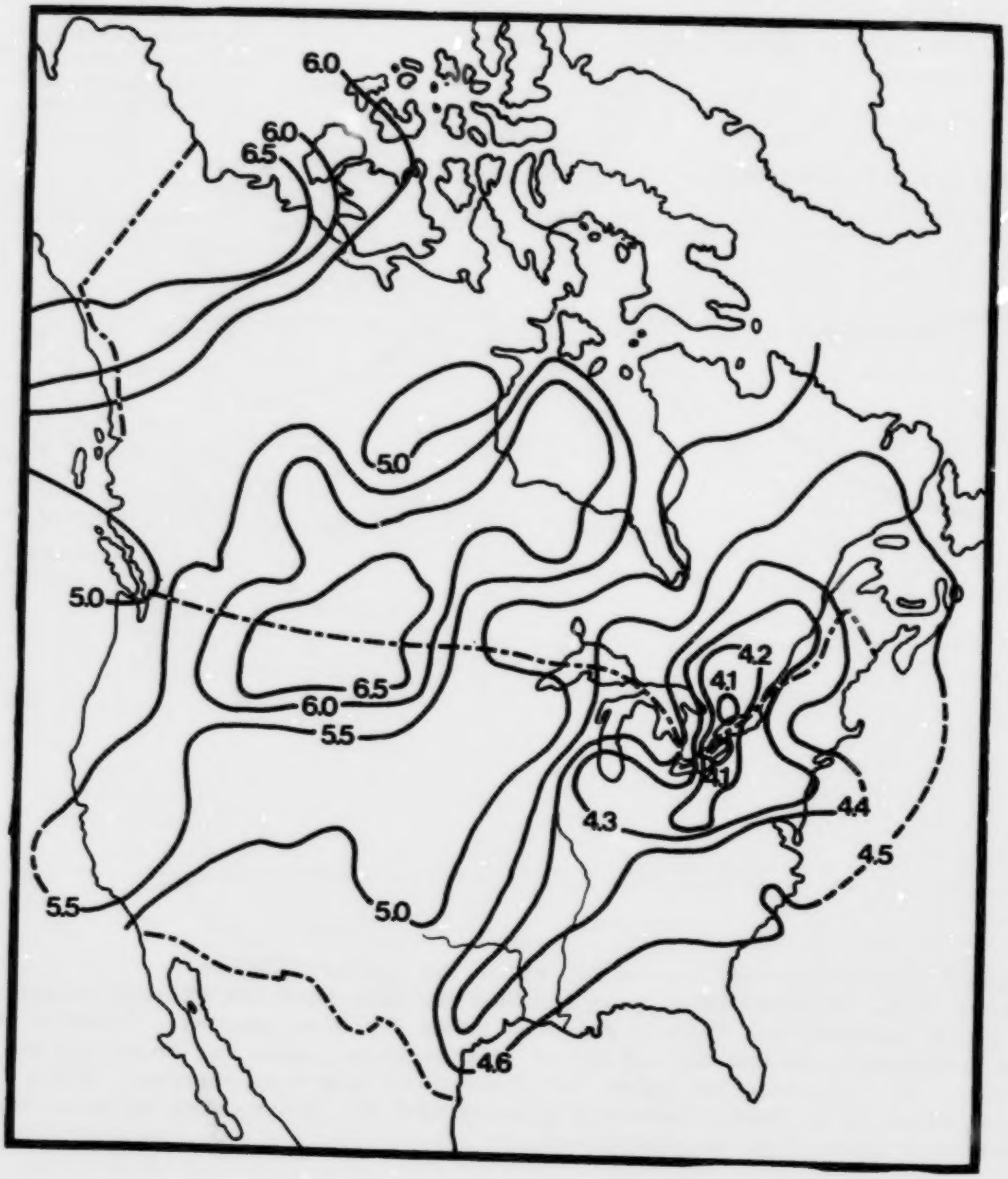


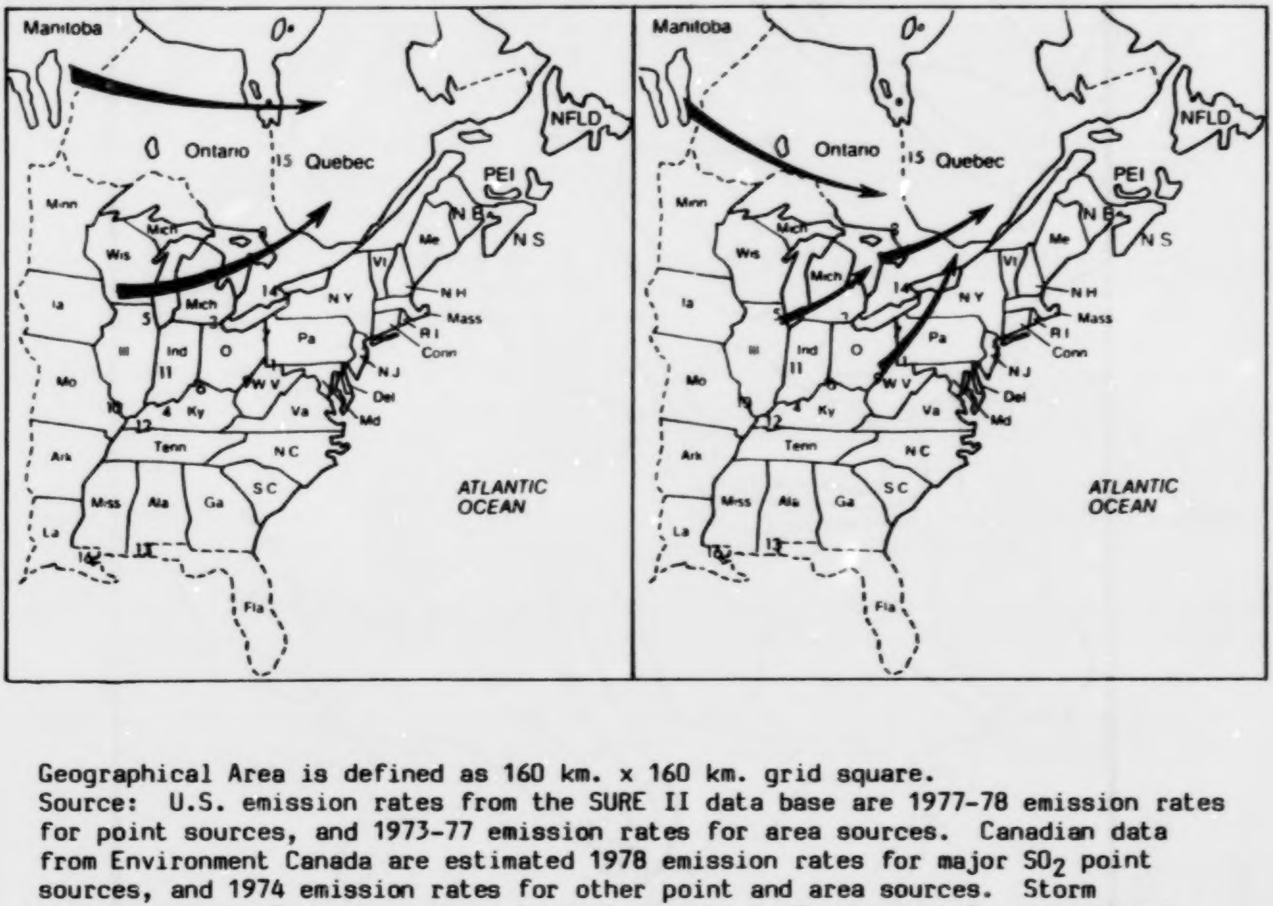
Figure 2.1 NATIONAL ATMOSPHERIC DEPOSITION PROGRAM - NC141
pH Annual Average - 1979
Precipitation-weighted
NADP & CANSAP DATA
February 1981

	Geographical Area	Grams/Second
1	East and West Pittsburg, Upper and Central Ohio River Valley	98,718.7
2	New York; New Jersey	81,892.2
3	Toledo, Ohio, Detroit, Michigan	65,421.6
4	Western Kentucky; South Indiana	53,623.7
5	Chicago, Illinois	53,040.7
6	Cincinnati, Ohio, North Kentucky	50,051.0
7	Cleveland, Ohio, West Pennsylvania	47,997.7
8	Sudbury, Ontario	43,915.3
9	Lower and Central Ohio, River Valley; Clarksburg, Virginia	42,401.3
10	East Montana, West Illinois	41,298.8
11	Indianapolis, Indiana	30,202.9
12	Western Kentucky	25,849.3
13	Mobile, South Alabama	24,138.5
14	Toronto, Ontario	18,584.7
15	Rouyn-Noranda, Quebec	16,402.2
16	Southern Louisiana	14,596.8

Important Storm Trajectories over Major SO_2 and NO_x Emitting Areas

FIG. 7 SUMMER

FIG. 8 WINTER



Geographical Area is defined as 160 km. x 160 km. grid square.
Source: U.S. emission rates from the SURE II data base are 1977-78 emission rates for point sources, and 1973-77 emission rates for area sources. Canadian data from Environment Canada are estimated 1978 emission rates for major SO_2 point sources, and 1974 emission rates for other point and area sources. Storm trajectories by J. Kurtz, meteorological scientist, Environment Ontario, based on 40 years of data, U.S. Weather Bureau.

(Adapted from O.M.O.E. 1980)

Figure 2.2 Eastern North America - Major SO_2 and NO_x Emitting Areas

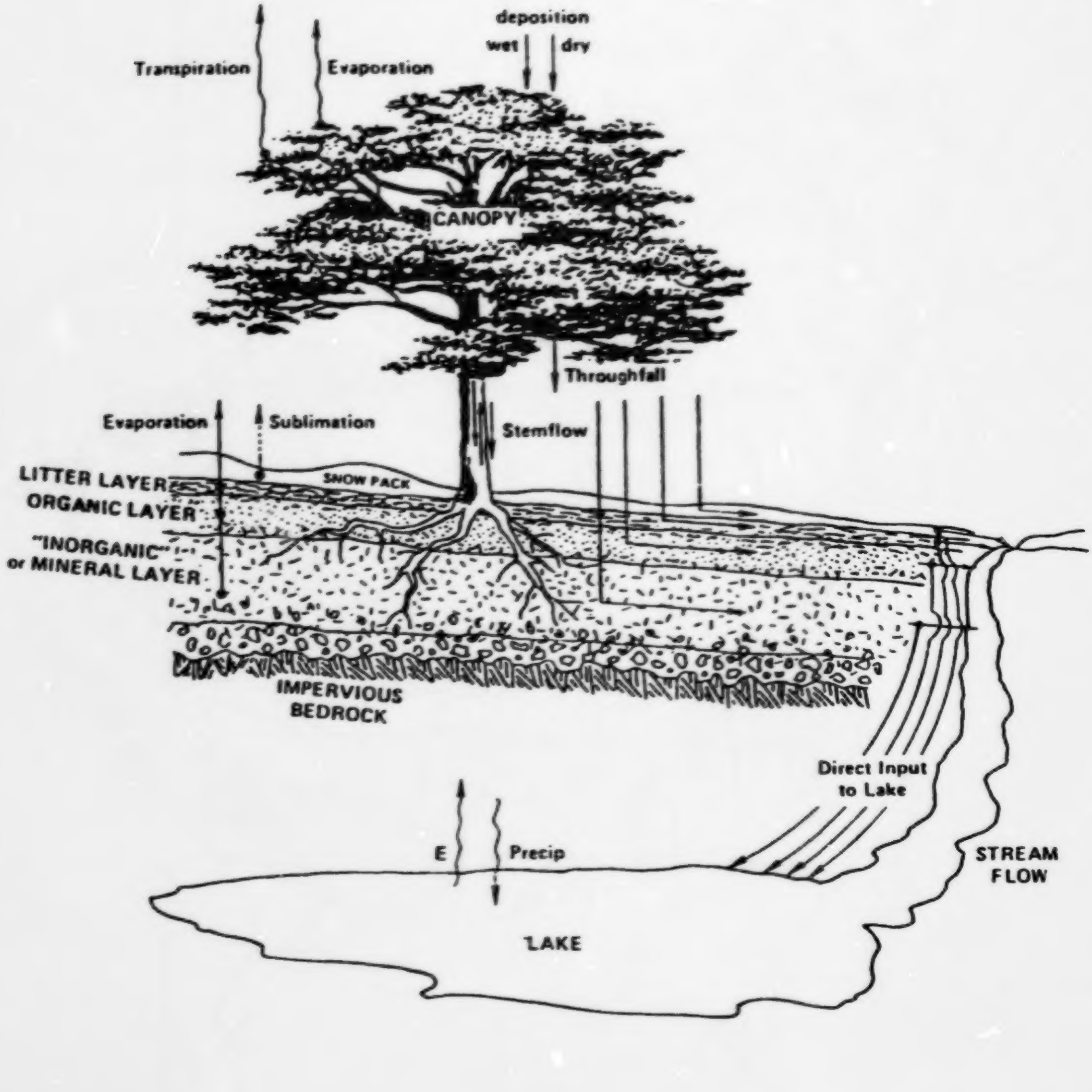


Figure 2.3 Definition sketch for the pathways of water tributary to a lake

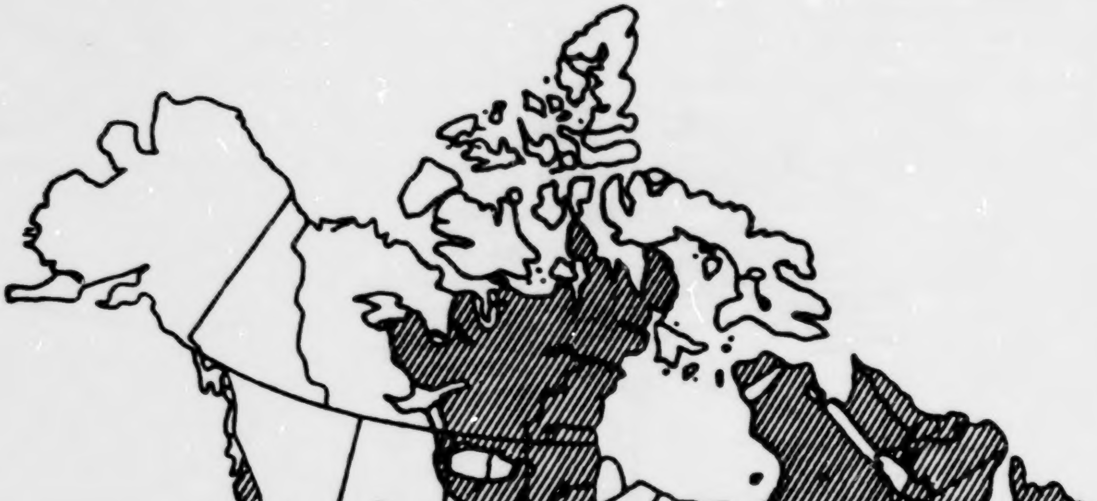
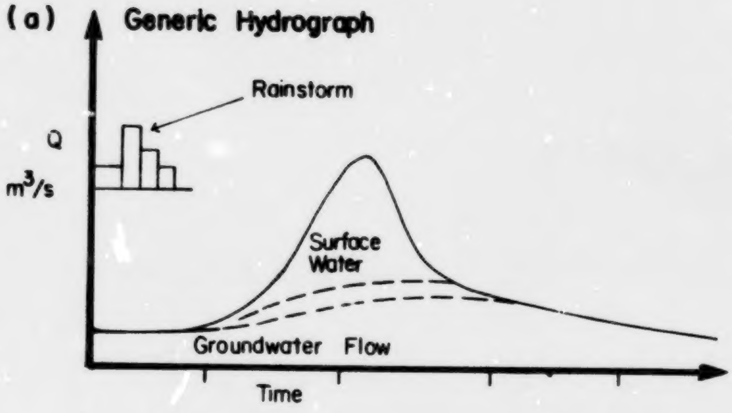
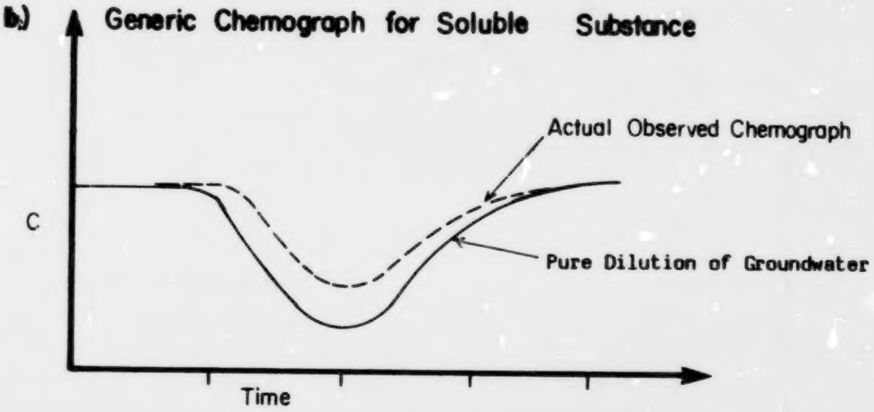


Figure 2.4 Regions in North America with lakes which may be sensitive to acid precipitation

(a) Generic Hydrograph



(b) Generic Chemograph for Soluble Substance



(c) Generic Chemograph for Particulate Substance

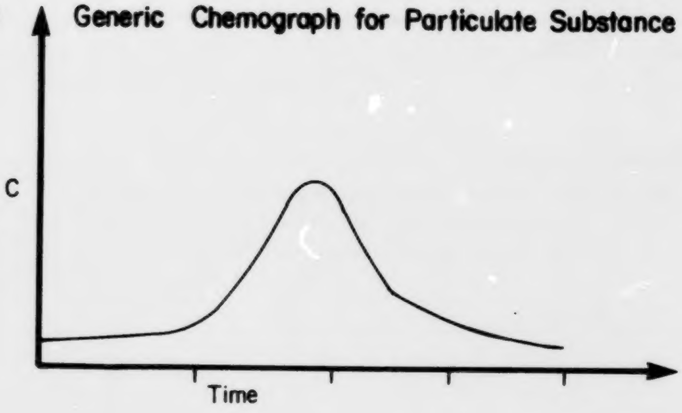
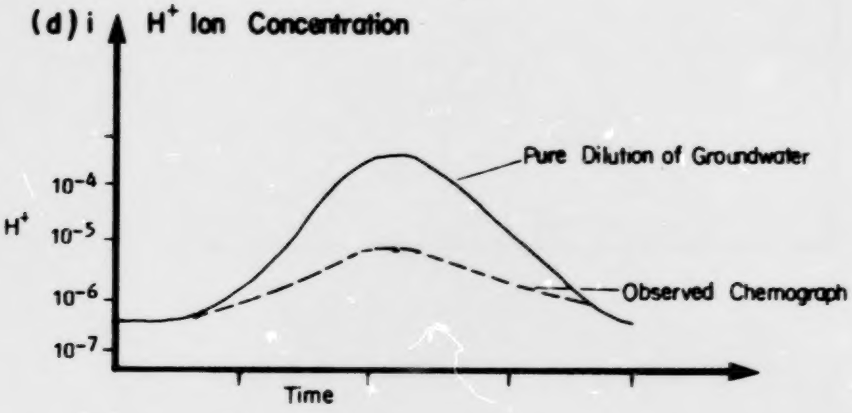
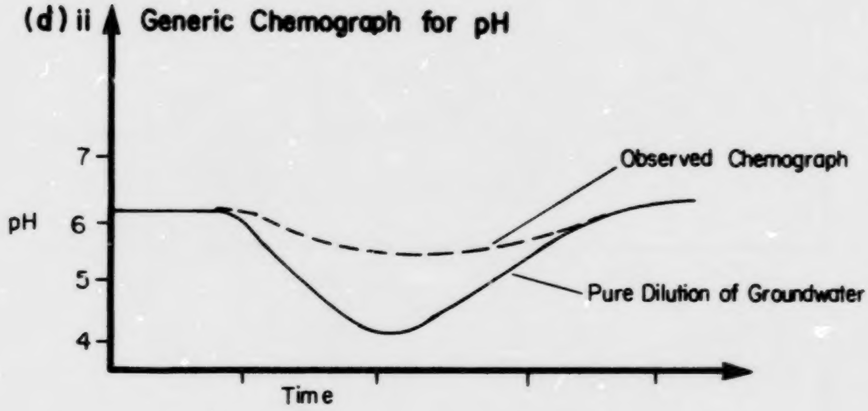
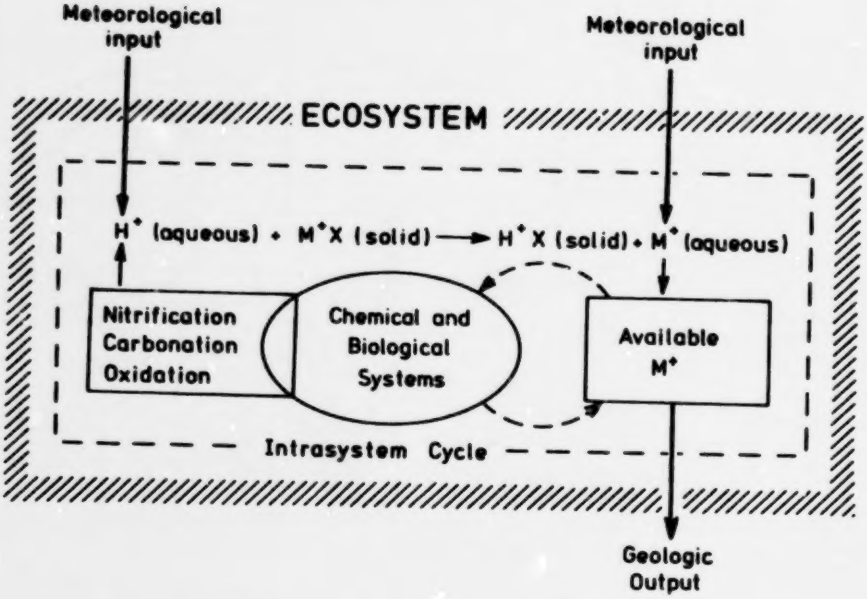


Figure 2.5 Generic Hydrograph and Chemograph

Figure 2.5


(d) i H$^+$ Ion Concentration


(d) ii Generic Chemograph for pH



M^+ represents a basic cation and X is an ionic exchange substrate, usually a primary silicate mineral, but also includes such derivatives as soil minerals or soil humates. The above illustrates that as H^+ is added to the system from external and internal sources, basic cations (M^+) are leached from the system, and primary silicate minerals (M^+X) are transformed into secondary minerals (H^+X).

Figure 2.6 Conceptual description of a watershed's weathering reaction (from Liken's et al., 1977)

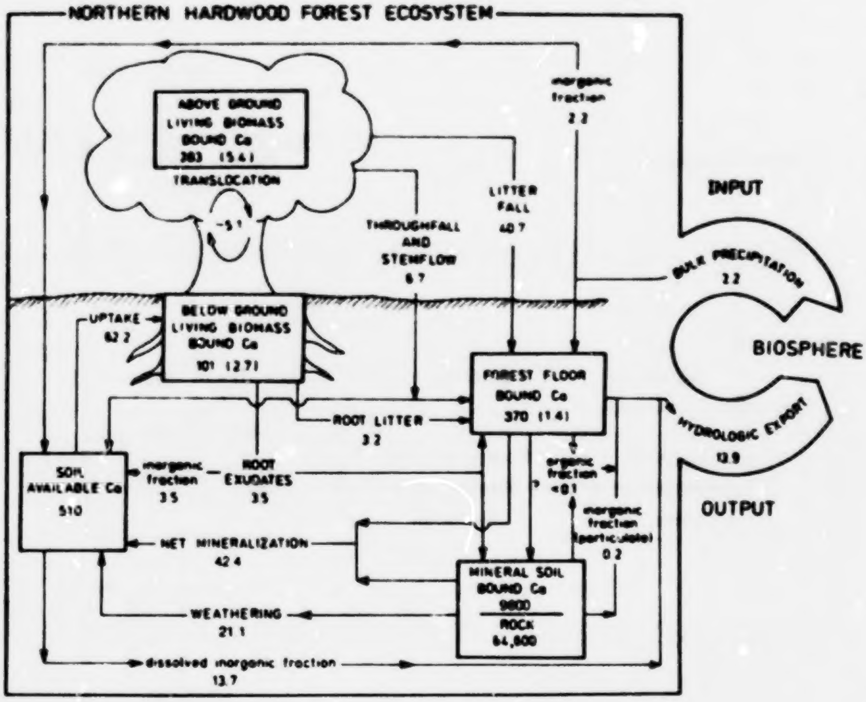

NORTHERN HARDWOOD FOREST ECOSYSTEM
ABOVE GROUND LIVING BIOMASS BOUND Ca 383 (5.4)
TRANSLOCATION
-5.1
inorganic fraction 2.2
LITTER FALL 40.7
THROUGHFALL AND STEMFLOW 6.7
INPUT
BULK PRECIPITATION 2.2
BIOSPHERE
UPTAKE 62.2
BELOW GROUND LIVING BIOMASS BOUND Ca 101 (2.7)
FOREST FLOOR BOUND Ca 370 (1.4)
ROOT LITTER 3.2
HYDROLOGIC EXPORT 13.9
SOIL AVAILABLE Ca 510
inorganic fraction 3.5
ROOT EXUDATES 3.5
organic fraction <0.1
OUTPUT
inorganic fraction (particulate) 0.2
NET MINERALIZATION 42.4
MINERAL SOIL BOUND Ca 9800
ROCK 64,800
WEATHERING 21.1
dissolved inorganic fraction 13.7

Figure 2.7 Annual calcium budget for an aggrading forested ecosystem at Hubbard Brook. Standing crop values are in kg/ha and calcium fluxes are in kg/ha.yr. Values in parentheses represent annual accretion rates.

Figures 2.7 and 2.8 Ecosystem Diagrams

General. The boxes within the diagram represent standing stocks or pools of elements. The values within these boxes are the size of the elemental pool and are in kg/ha. Because the Hubbard Brook Forest is an aggrading ecosystem with an annual net accumulation of biomass, the rate at which the element is accumulating each year is given in parentheses within the appropriate box in kg/ha.yr. The arrows between the various pools represent annual fluxes and are given in kg/ha.yr.

The last cutting of the forest at Hubbard Brook took place between 1909 and 1917. Indications are that the majority of the cutting took place closer to 1917 than to 1909. Therefore, we are making the assumption that forest regrowth was initiated around 1915. The majority of the measurements, which form the basis for the diagrams, were made around 1970. Where the age of the forest was needed (e.g., in the calculation of forest floor accretion) 55 yrs. was used.

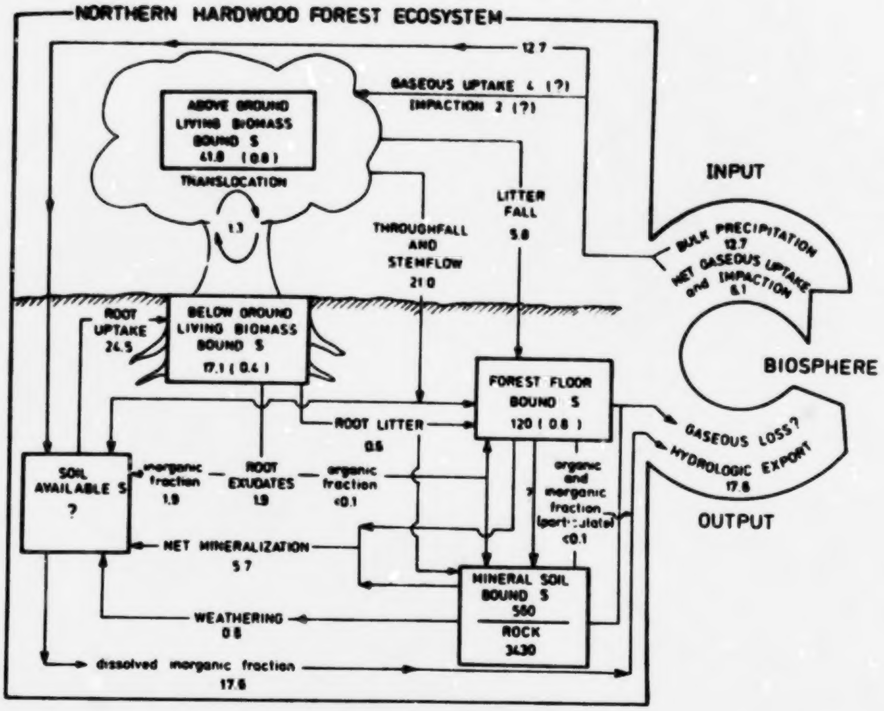
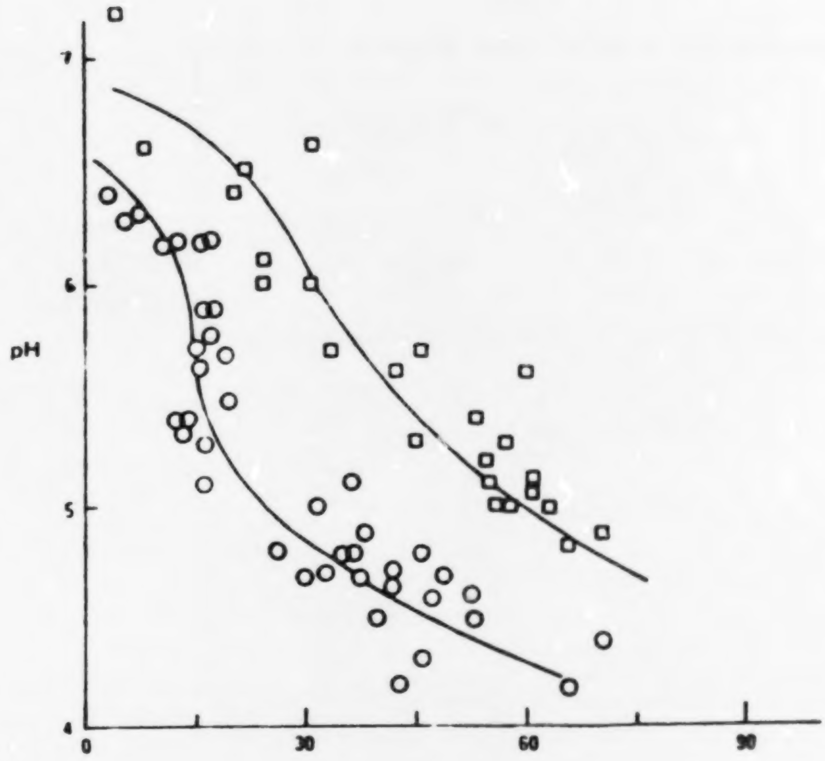


Figure 2.8 Annual sulfur budget for an aggrading forested ecosystem at Hubbard Brook. Standing crop values are in kg/ha and sulfur fluxes are in kg/ha.yr. Values in parentheses represent annual accretion rates.



SULFATE LOADING TO LAKE WATER (Kg/ha/yr)

Figure 2.9 Relationship between acid loading and pH change for:

0 very sensitive and

☐ moderate sensitive surroundings

(From GCA, 1980)

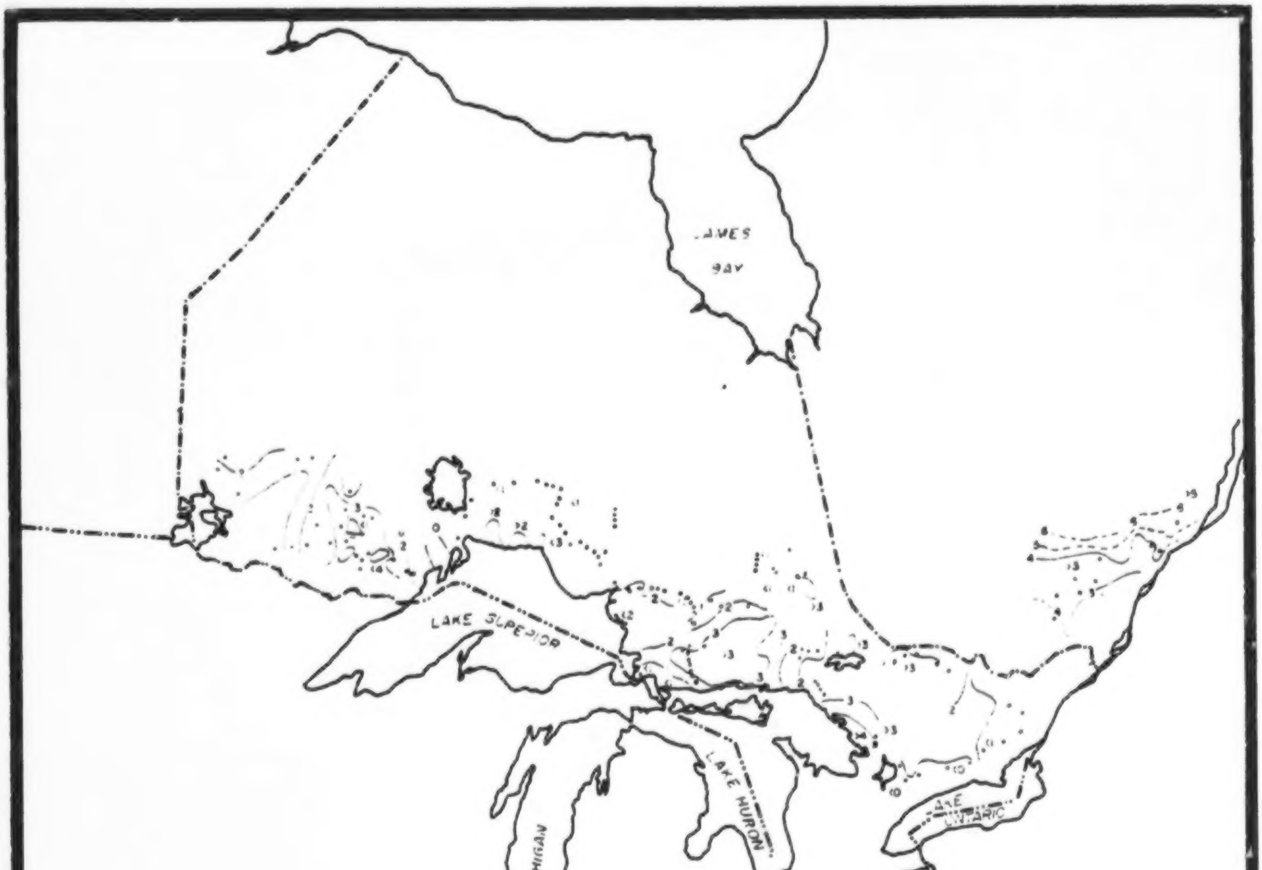


Figure 2.10 Calcite saturation index (CSI) for portion of Quebec and Northern Ontario. A dot represents a sampling site. Areas with CSI greater than 3 or 4 are susceptible to pH depression below 5 after acidification. Particularly susceptible areas are the Rainy River-English River District, the Muskoka-Algonquin Park area and the Algoma District in Eastern Ontario and the portions of Quebec shown on the map (after Kramer, 1979).

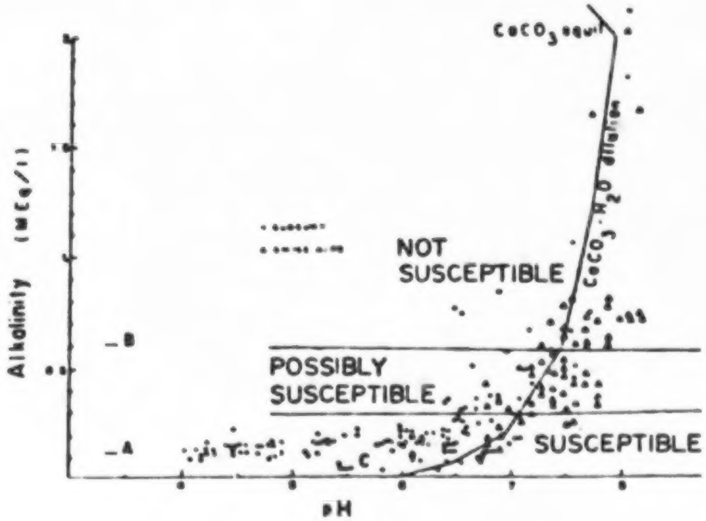


Figure 2.11 pH alkalinity relationship for lakes in the Canadian Shield and Swiss Alps. The solid line represents the dilution of water equilibrated with $CaCO_3$ at 2 meg/1 carbonate alkalinity. A and B represent pH boundary values for alumino silicate control whereas C represents the alkalinity pH obtained from $FeOOH-H_2O-CO_2$ (atm) equilibrium. (From Kramer, 1977)

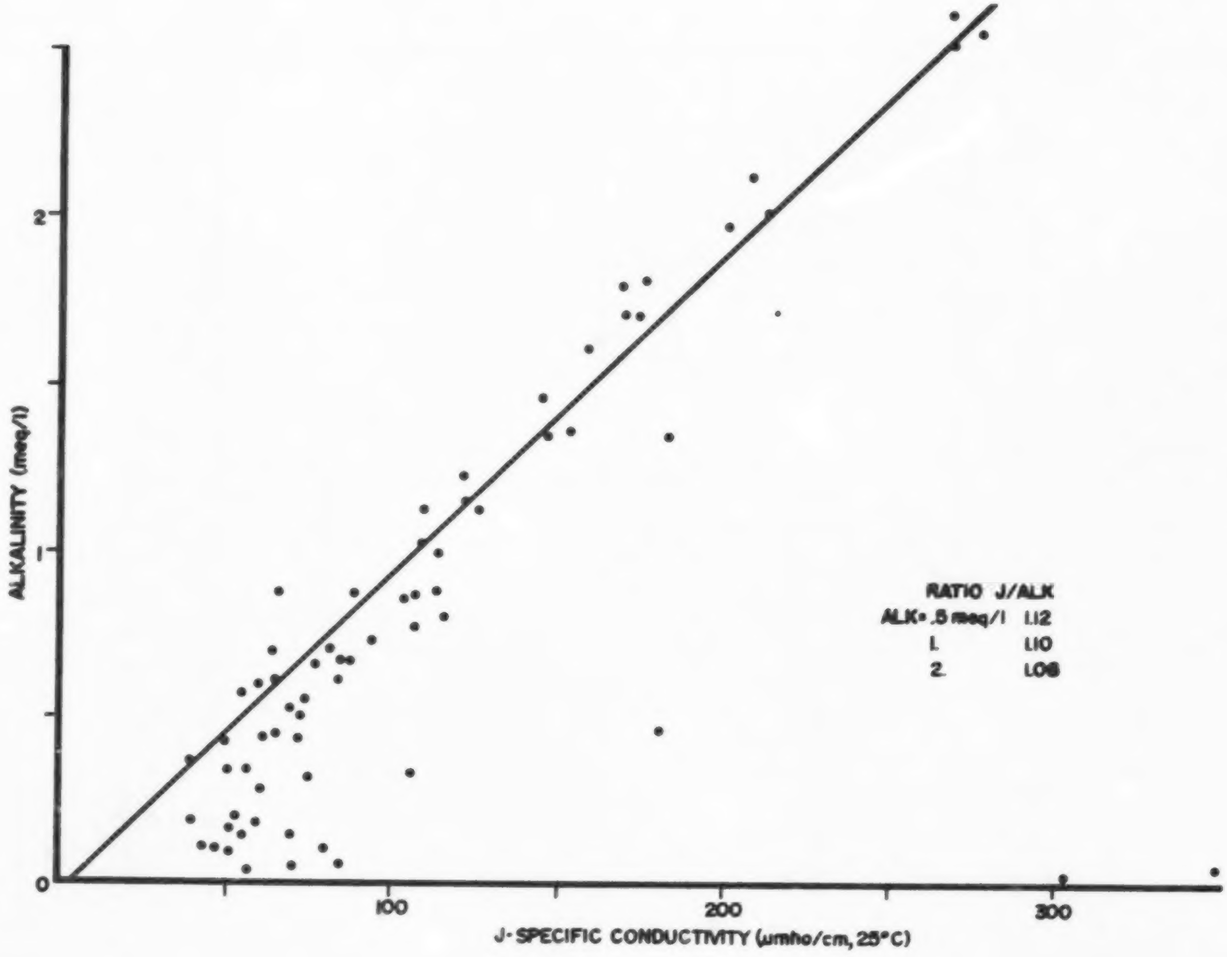


Figure 2.12 Relationship of specific conductivity and alkalinity of streams and lakes. The line is obtained from ionic conductivities for Ca and HCO_3 ions. The data points fit the simple model well. (from Kramer, 1977)

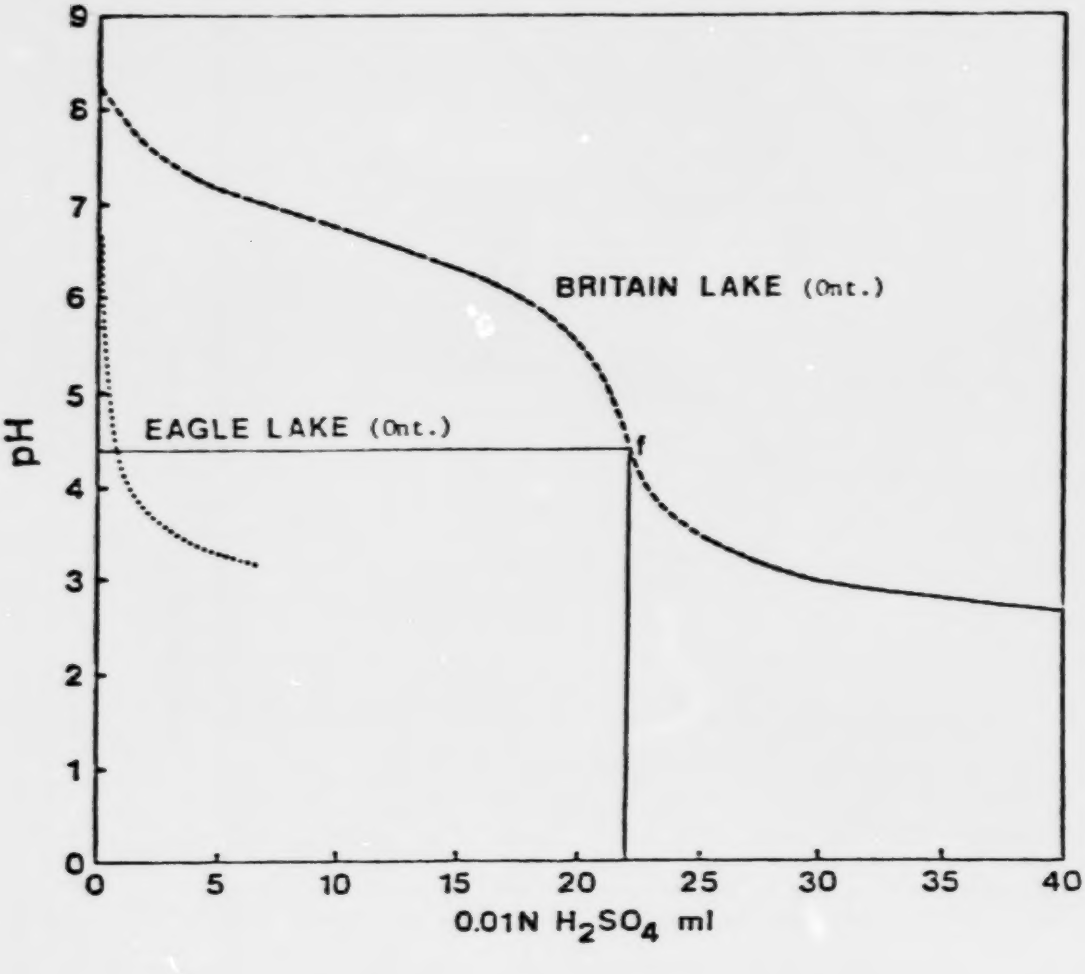


Figure 2.13 Alkalinity titration curves for one soft-water and one hard-water lake. Note the rapid decline in pH in Eagle Lake on addition of a small amount of acid (from Zimmerman and Harvey, 1979)

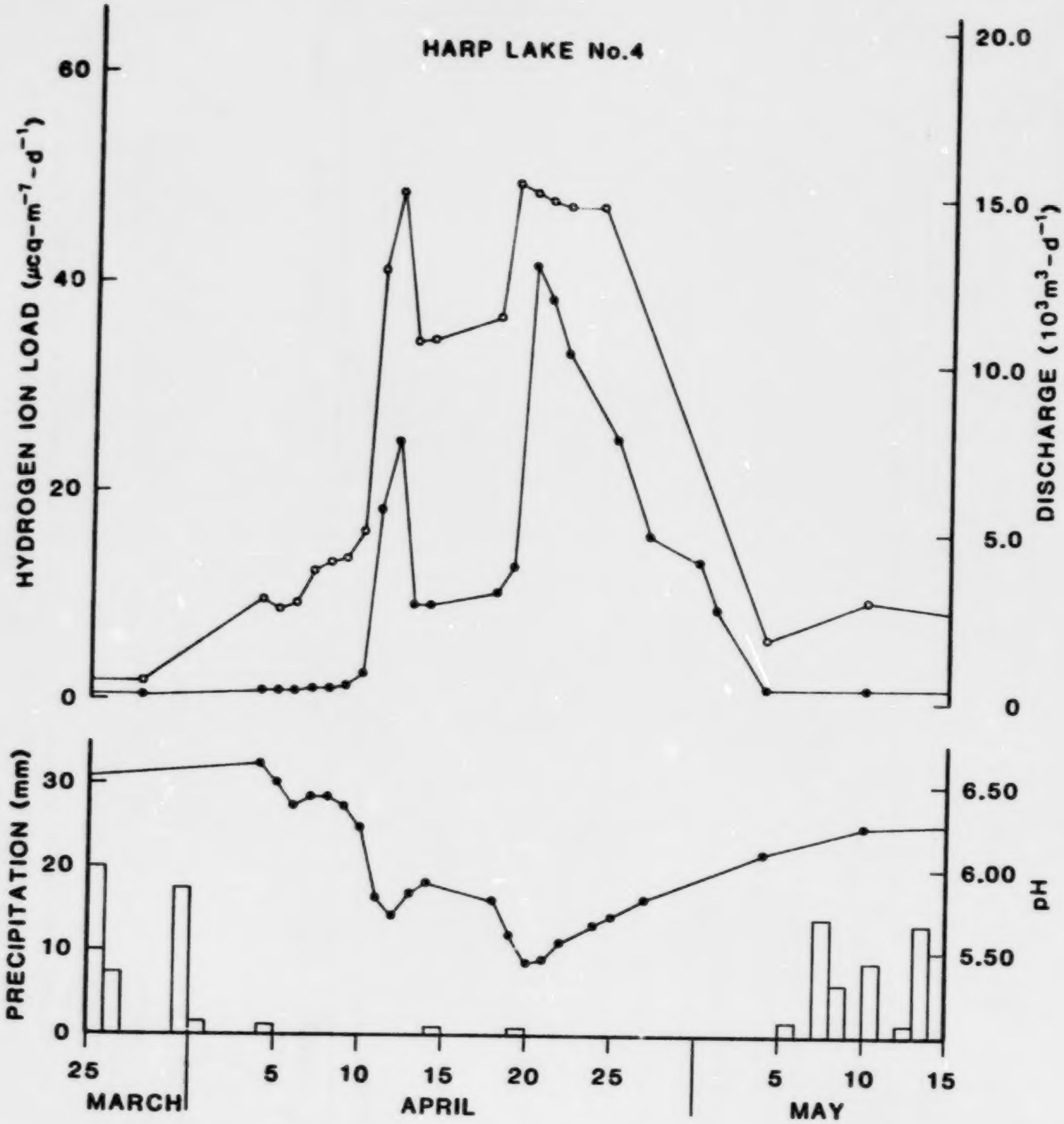


Figure 2.14 "Spring pH Depression" of a Stream
Graph illustrating "spring pH depression" in one of the six inflowing streams to Harp Lake, a study lake in Muskoka. As the spring runoff increases the amount of water, the acidic melted snow causes the stream pH to drop, producing severe chemical "shock" effects on aquatic life. (OME, 1981)

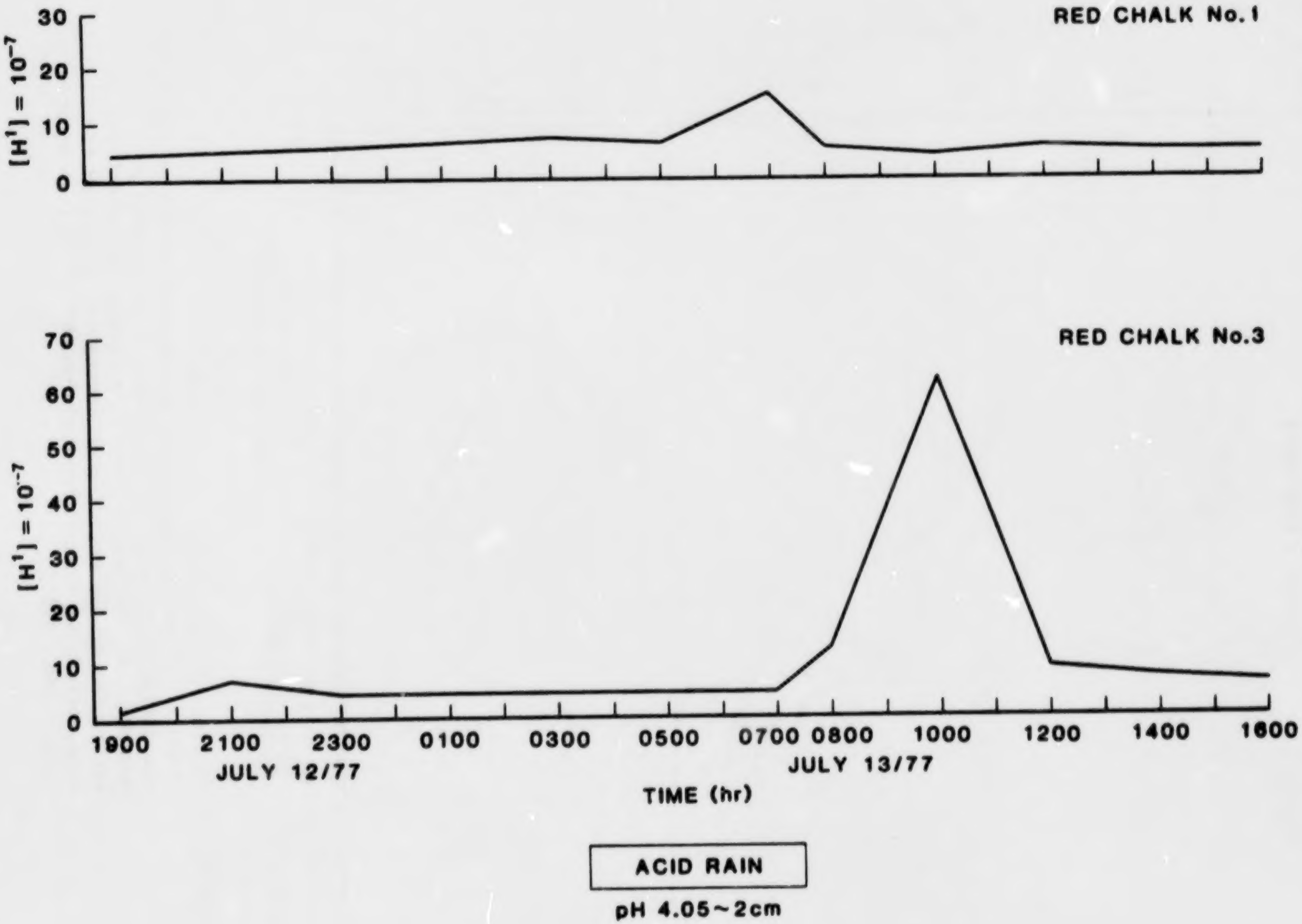


Figure 2.15 Hydrogen ion content of streams draining Red Chalk Lake watersheds No 3 and No 1 (Dorset, Ontario) showing effects of a 2 cm rainfall (pH 4.06) between 11:00 p.m. July 12 1977 and 3 00 a m. July 13 1977 (OME 1981)

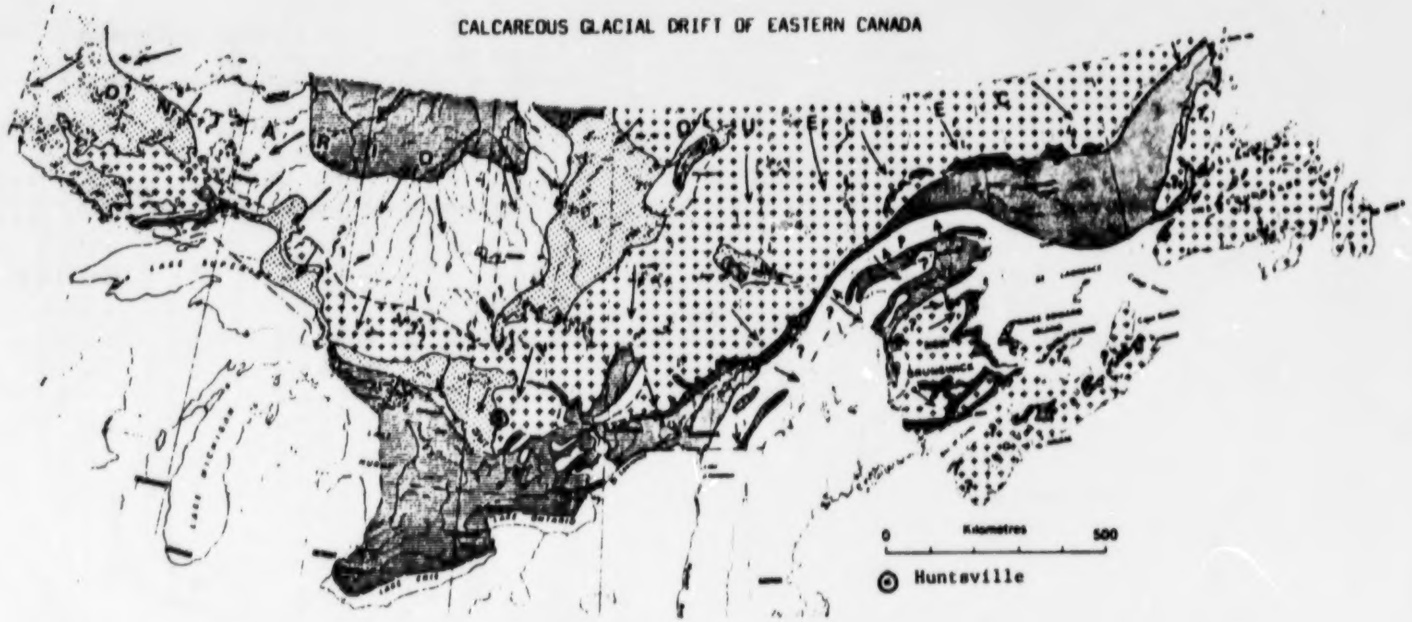


Figure 3.1 SENSITIVITY OF GLACIAL AND POSTGLACIAL SURFICIAL SEDIMENTS TO ACID LOADING*

INDETERMINATE OR INTERMEDIATE SENSITIVITY

▥ Areas formerly submerged beneath postglacial seas; high probability of occurrence of calcareous, fine-grained marine sediments

▒ Areas formerly submerged beneath proglacial lakes; high probability of occurrence of calcareous, fine-grained lake sediments

□ Areas of calcareous drift, glacially transported from major carbonate outcrops; shown only where known or suspected.

LOW SENSITIVITY

▤ Areas underlain by carbonate bedrock; all surficial deposits likely to be calcareous

HIGH SENSITIVITY

⁺ Areas where surficial deposits are likely to be non-calcareous.

* Local buffering capacity in these generalized areas is proportional to thickness of surficial deposits. Less surficial sediment equals less buffering capacity.

Approximate limit of individual glacial trains of significant carbonate debris .... - - -

Generalized direction of glacial transport...... →

Areas where limits of glacial dispersal of carbonate bedrock are not well known.. ....?

(From Altschuller, McBean, 1980)

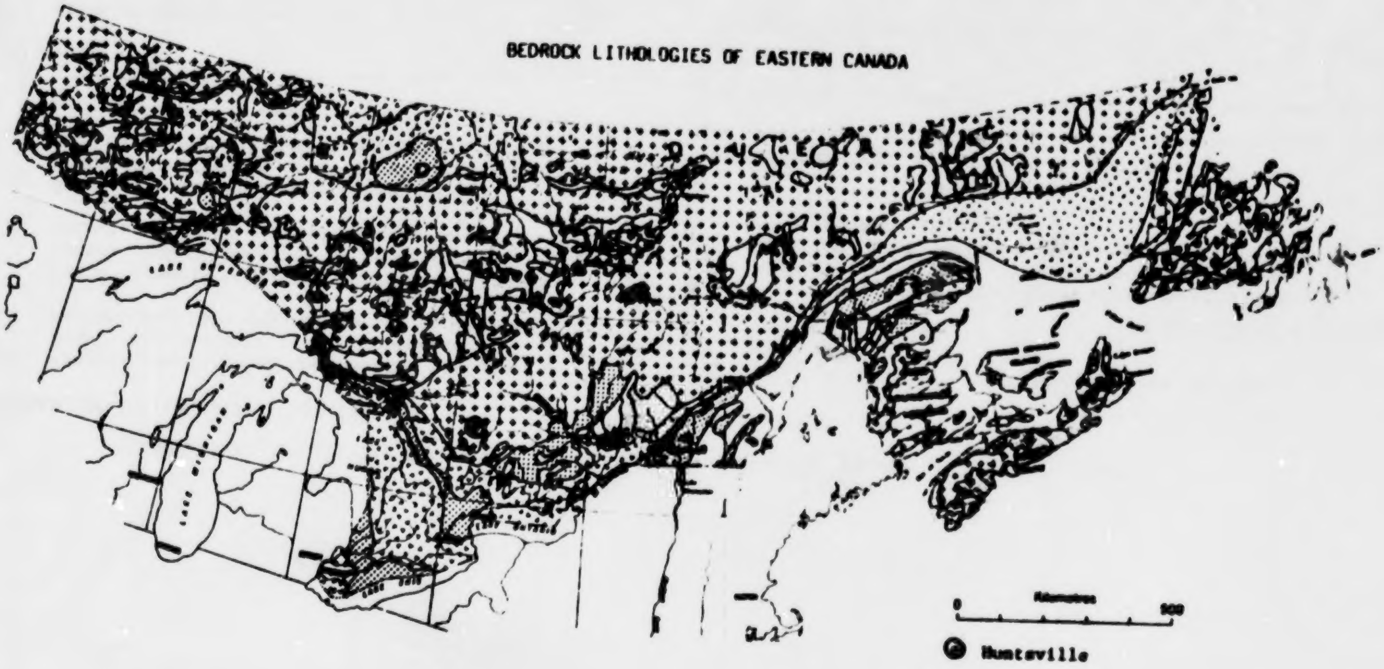


Figure 3.2 ACID PRECIPITATION SENSITIVITY-BEDROCK AND SOILS DERIVED FROM BEDROCK
(Altschuller, McBean, 1980)

HIGH SENSITIVITY

✚ Granite, granite gneiss, orthoquartzite, syenite

INTERMEDIATE-HIGH SENSITIVITY

☐ Volcanic rocks, shales, greywacke sandstones. ultramafic rocks, gabbro, mudstone, and metamorphic equivalents

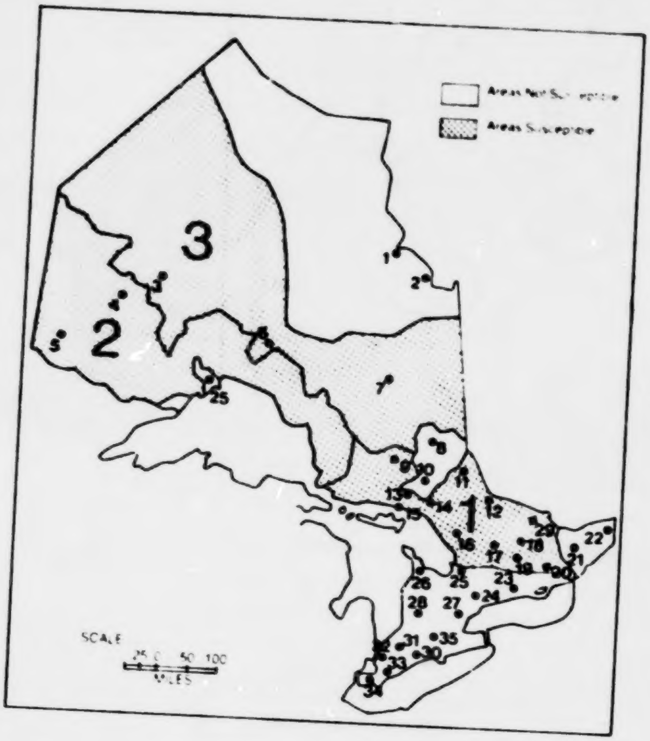
INTERMEDIATE-LOW SENSITIVITY

▒ Calcareous clastic rocks, carbonate rocks interbedded or interspersed with non calcareous sedimentary, igneous and metamorphic rocks

LOW SENSITIVITY

⁙ Limestone, dolomite and metamorphic equivalents

Figure 4.1 Locations of Ontario's Acid Rain Monitoring Sites*



* Cumulative Sites - monitored monthly

1. Attawapiscat
2. Moosonee*
3. Pickle Lake
4. Ear Falls
5 Experimental Lakes Area*
6. Nakina
7. Moonbeam
8. Gowganda
9. Ramsey
10. Hanmer
11. Bear Island
12. Mattawa
13. Lively
14. Burwash
15. Killarney
16. McKellar
17. Dorset
18. Whitney
19. Wilberforce
20. Kaladar
21. Smiths Falls
22. Dalhousie Mills
23. Campbellford
24. Uxbridge
25. Dorion
26. Shallow Lake
27. Milton
28. Palmerston
29. Golden Lake
30. Pt. Stanley
31. Alvinston
32. Wilkesport
33. Merlin
34. Colchester
35. Waterloo

Note
* Proposed sites

Daily "Event" Network

The "event" network is located in the vicinities of London, Dorset and Kingston, with each centre having five collection or monitoring sites clustered within a radius of 50 to 100 kilometres. The Dorset location was chosen because of the major acid rain studies already in progress there. The London and Kingston areas were chosen to provide information on the contribution to local acidic deposition from major northeastern continental sources.

This network utilizes highly sensitive equipment at each of its 15 monitoring sites for the sampling of atmospheric pollutants. The instrumentation is specifically designed to sample particulates and gaseous sulphur and nitrogen compounds for 24-hour periods.

The daily data generated from monitoring and sampling at these centres, when coupled with relevant meteorological data, such as surface and upper level weather observations, can aid in the identification of the major continental sources contributing to acidic precipitation in Ontario. The necessary meteorological data are obtained by the Ministry directly through a computer link with the Atmospheric Environment Service of Environment Canada.

"Cumulative" Monthly Network

The "cumulative" network consists of 30 sites, ranging in location from the Windsor area northwest to the Kenora region and northeast to James Bay, southward down the Ottawa River, and westward to sites scattered throughout south central Ontario.

Each of these monitoring stations is equipped with automatically operated "double bucket" collectors to measure the accumulated "wet" and "dry" deposition, with samples collected monthly for laboratory analysis. In addition, 20 of these stations are equipped with instrumentation to collect monthly samples of particulate sulphate, nitrate, ammonium and gaseous SO_2 in their immediate vicinity.

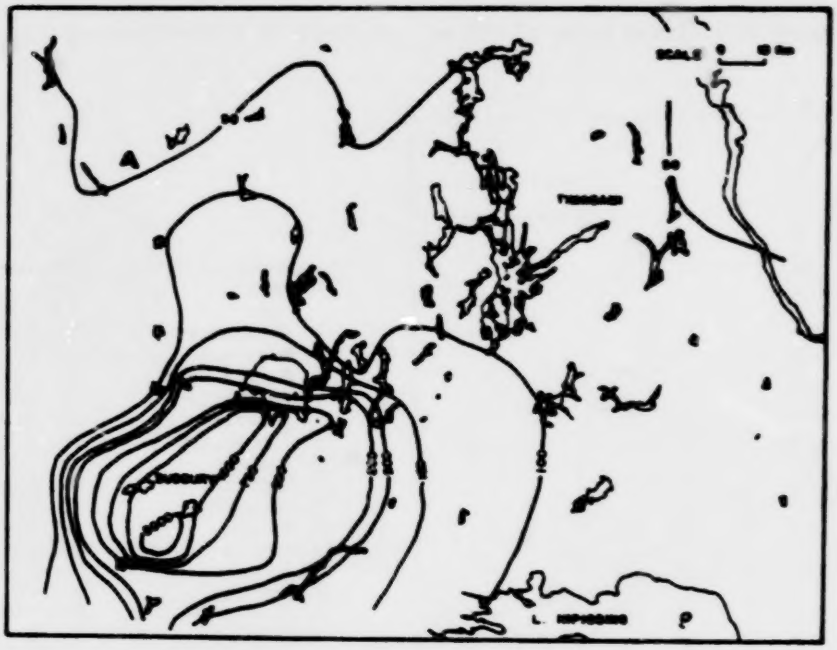


Figure 4.2a. Areal distribution of nickel (µg/g. dry weight) in bottom sediments of Sudbury, Ontario area lakes (Sempkin, 1975)

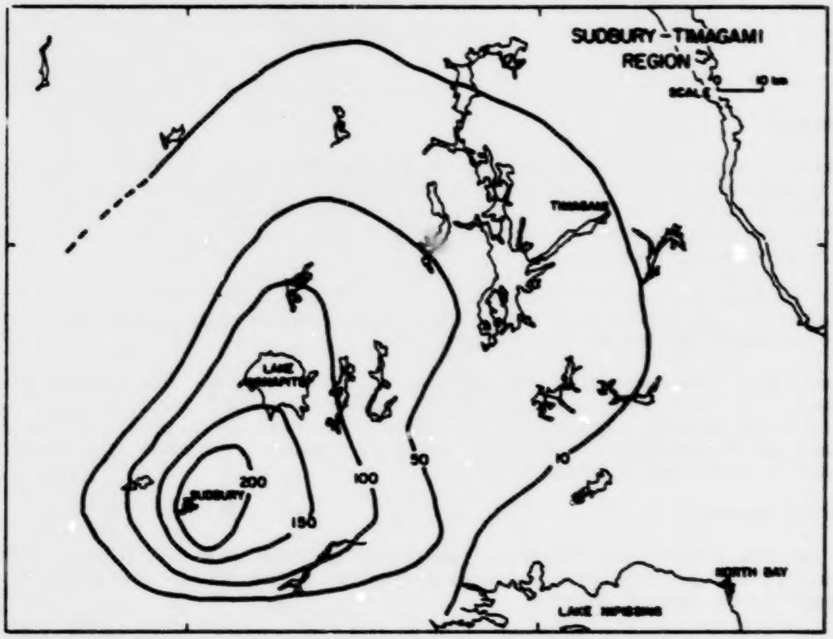


Figure 4.2b. Areal distribution of nickel (µg/ℓ) in atmospheric precipitation adjoining Sudbury, Ontario (Sempkin, 1975)

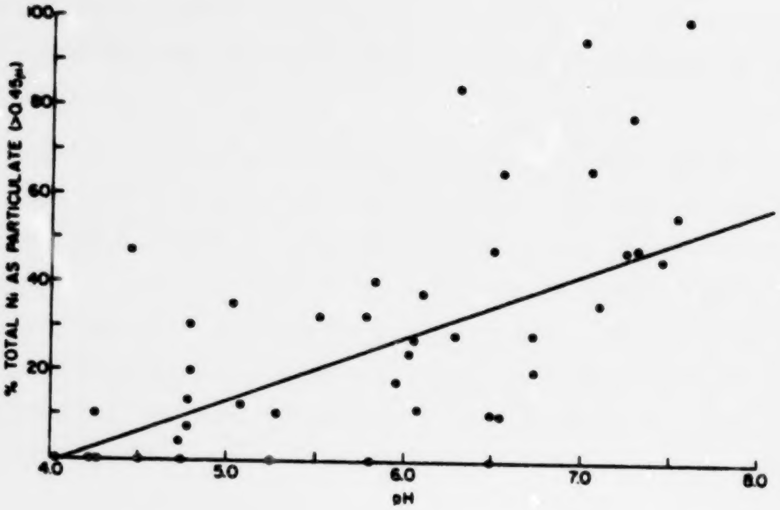


Figure 4.2c. Soluble nickel as a function of pH in surface/composite waters of Sudbury, Ontario area lakes (after Sempkin, 1975)

ASPECTS OF ALKALINITY TITRATION CURVE
(from Zimmerman and Harvey, 1979)

Buffering capacity is the ability of a system to resist shifts in pH upon addition of acid or base. It is expressed numerically by differentiating the equation which defines the titration curve with respect to pH. When the titrant is a strong acid the capacity that is being measured is with respect to decreases in pH and is called alkalinity.

The precision of the determination is dependent upon two factors - the definition of a reference proton level (the equivalence point) and recognition of that endpoint in the actual titration. The ability to define the reference proton level or equivalence point in natural waters depends upon the magnitude of dissolved buffer components other than carbonates and the carbon concentration. In a pure carbonate solution, alkalinity is simply a function of total inorganic carbon concentration $[C_T]$ (corrected for the ionized fractions, bicarbonate, α_1, and carbonate α_2) plus the hydroxyl concentration $[OH^-]$ minus the proton concentration $[H^+]$ or

$$\text{Alk} = [C_T](\alpha_1 + 2\alpha_2) + [OH^-] - [H^+]$$

In a mixed solution, terms must be added for each additional buffering agent. For example, ammonia is often a significant buffering agent in anaerobic water, hence alkalinity must now be defined as

$$\text{Alk} = [C_T](\alpha_1 + 2\alpha_2) + [NH_3] + [OH^-] - [H^+]$$

The ability to recognize the endpoint is related to both the ionic strength of the solution being titrated (the more dilute the solution, the more difficult the endpoint is to recognize) and the method used to detect that endpoint, be it visual, potentiometric or conductimetric.

G. Gran (1952) has developed a graphical method of endpoint location for potentiometric titrations based on the fact that added increments of mineral acid increase the hydrogen ion concentration in a linear fashion.

In a plot of pH against the volume of acid added (see Figure A.2) the endpoint (f) or $[H_2CO_3] \rightleftarrows [H^+]$ equivalence can be found by plotting the total volume of sample + acid increments corrected for hydrogen ion concentration (the Gran function -10^{-pH} Vs + Va) against Va - the cumulative volume of acid.

f becomes a function of the slope (b) and intercept (a) of the Gran transformation plot or $f = \frac{-a}{b}$

The alkalinity becomes a function of 1.) endpoint point (which subsumes the total concentration of all buffering species or the right side of the alkalinity equations) 2.) the normality of acid (N) and 3.) the sample volume (v_s): or $Alk = \frac{f\ (N)}{Vs}$

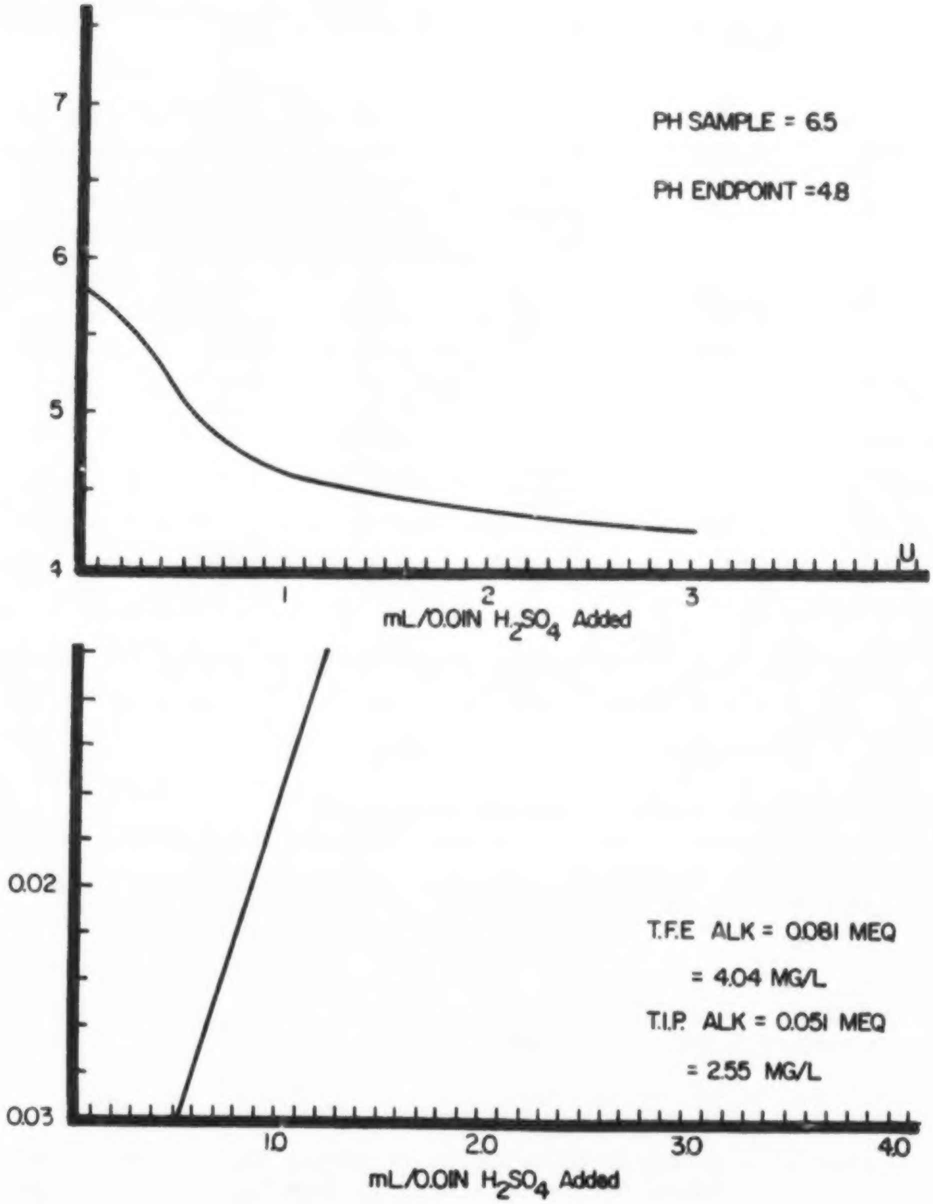
As an aside, note how difficult f is to locate on the titration of Eagle Lake. Figures A.1 and A.2 illustrate methods of treating acqual titration data. Figure A.2 is used when a plot of pH against acid has been generated automatically in the laboratory where the system is much more elaborate than in the field. Figure A.1 is a regression analysis of the Gran function plot for slope/intercept determination and is used when titration data are taken directly from the pH meter in the field. In Figure A.2 it can be seen that a fixed endpoint of 4.5 (TFE alkalinity) would lead to an alkalinity of 4.04 mgL^{-1} (80 μeqL^{-1}), while the actual alkalinity (TIP) is 2.55 mgL^{-1} or 51 μeqL^{-1}. This value compares with 47.9 generated by regression.

Comparison of lab determinations, which are closed systems to prevent volatilization of H_2CO_3 (as CO_2), with open container titrations as done in the field, show that relative CO_2 losses are not significant when the samples are stirred uniformly.

```
                    SAMPLE IDENTIFICATION - N2A2 EAGLE

NUMBER OF SAMPLE PAIRS = 17
VS VALUE               = 100.1


          VA      PRED F1      CALC F1       pH       LOW F1      HIGH F1


         0.75      0.003        0.003       4.500      0.003        0.004
         0.90      0.005        0.005       4.300      0.004        0.006
         1.05      0.007        0.006       4.200      0.006        0.007
         1.20      0.009        0.008       4.100      0.008        0.009
         1.35      0.010        0.010       4.000      0.010        0.011
         1.50      0.012        0.011       3.950      0.011        0.013
         1.65      0.014        0.014       3.850      0.013        0.015
         1.82      0.016        0.016       3.800      0.015        0.016
         1.95      0.018        0.020       3.700      0.017        0.018
         2.10      0.019        0.020       3.700      0.019        0.020
         2.25      0.021        0.020       3.700      0.020        0.022
         2.40      0.023        0.023       3.650      0.022        0.024
         2.55      0.025        0.023       3.650      0.024        0.026
         2.70      0.026        0.026       3.600      0.026        0.027
         2.85      0.028        0.029       3.550      0.027        0.029
         3.00      0.030        0.029       3.550      0.029        0.031
         3.15      0.032        0.033       3.500      0.031        0.033

VE VALUE  =   0.4798 COEFFICIENT OF VARIATION FOR VE = 0.12969

A VALUE   =  47.9801

SLOPE VALUE =  0.011927 LIMITS  0.011188 TO 0.012667
INTERCEPT   =  0.005723
CORRELATION COEFFICIENT =  0.99371
STANDARD DEVIATION OF F1 ON VA =  0.001052

VARIANCE (SLOPE)          =  0.12045D-06
VARIANCE (INTERCEPT)      =  0.52307D-06
VARIANCE (-INTERCEPT/SLOPE) -  0.003872
```

Figure A.1 Computer calculation of alkalinity for Eagle Lake based on the data read in from the Gran titration.

Eagle Lake (A)
May 25, 1978



PH SAMPLE = 6.5

PH ENDPOINT = 4.8

T.F.E ALK = 0.081 MEQ

= 4.04 MG/L

T.I.P. ALK = 0.051 MEQ

= 2.55 MG/L

Figure A.2 Machine-plotted alkalinity curve and calculated intercept MOE technique. Total free alkalinity is 81 micro equivalents (from Zimmerman and Harvey, 1979).

A REVIEW OF THE LITERATURE ON THE INFLUENCE OF pH ON THE MICROBIOLOGICAL QUALITY OF COMMUNITY WATER SUPPLIES

In preparing this literature review on the influence of pH on the quality of community drinking water supplies several papers in addition to those quoted in the text of this review were consulted. Studies of bacterial populations in surface waters, acidic from mine tailings, often concentrate on the species and relative abundance of sulphur, nitrogen, and iron cycle bacteria. Although these bacteria may cause unpleasant taste and odour problems in community drinking water supplies, they are not considered pathogenic. To date, most of the material published on waterborne pathogens originates in the United States. Reference in this report to organisms implicated in waterborne illnesses will refer to those identified in the United States unless otherwise indicated.

At present, information directly related to the effects of pH on the quality of community drinking water supplies is scant. In isolated studies, the effects of pH on the species and numbers of microorganisms inhabiting unpolluted streams (15,17) microbial virulence (11,14), and the critical dosage of chlorine required to kill test organisms (3,5) have been investigated. Summaries of the diseases reported in the United States which are attributed to contaminated drinking waters are prepared annually by the Center for Disease Control (CDC) in Atlanta (4). A similar summary is available for Canadian waterborne diseases from the Bureau of Microbial Hazards of Health and Welfare Canada in Ottawa.

According to a report by the Safe Drinking Water Committee in the United States there are three principal groups of microorganisms implicated in waterborne diseases: bacteria, viruses, and protozoa. Although yeasts and fungi can be isolated from surface waters, very little information is available concerning the activities of the pathogenic species in drinking waters. Undesirable tastes and odours in drinking waters may be associated with fungi and/or algae.

Table 1 presents the diseases transmitted by community water supplies in the United States for the years 1946-1974 (19). The majority of the waterborne illnesses were reported as gastroenteritis of unknown origin. Since the late 1960s three etiologic agents: Giardia lamblia, Yersinia enterocolitica, and enteropathogenic E. coli have been isolated with increasing frequency from similar cases of gastroenteritis.

Generally, bacteria grow over a narrow pH range of 3 to 4 units. For example, Salmonella typhosa has an optimum pH of 6.5 to 7.2 but will grow over the pH range of 4.5 to 8.0 (9). Similarly, E. coli will grow at a minimum pH of 4.4 to a maximum of 9.0, but prefers 6.0 to 7.0 (9). Legionella pneumophila, the bacterium responsible for Legionnaires Disease and isolated from air conditioner cooling waters has a very narrow pH range of 6.3 to 7.1 with an optimum pH of 6.7 to 6.9 (10).

Fungi and yeasts are able to grow over a much wider pH range than are most bacteria. Molds as a general class of organisms can tolerate pH values as low as 2.0 and as high as 9.0, but prefer a pH approximating 5.6. Individual species may show preferences for more acidic, neutral, or alkaline conditions. Yeasts grow over a similar pH range of 2.0 to 8.0, but generally prefer a more acidic pH of 3.5 to 3.8 (9).

Viruses also are more resistant to low pH levels than are bacteria. They are protected by a resistant proteinaceous coat. The most important human enteric viruses are the enteroviruses, reoviruses, parvoviruses, and the adenoviruses. All are considered acid-stable (18). Viral agents of gastrointestinal illnesses are also more resistant to disinfectants than are the bacterial agents.

Bick and Evans (2) investigated the effect of acidification on the populations of bacteria and protozoa associated with peptone decomposition. As the pH dropped from 7 to 5, the total counts of bacteria as well as the number of species of ciliated protozoa decreased slowly. A further reduction in pH from 5 to 3 reduced bacterial numbers and protozoan species more rapidly.

Studies to determine the pH range of a particular microorganism are often executed in the laboratory using pure cultures. As conditions in the laboratory seldom approximate those in the environment, factors not considered in the in vitro experiments may affect the growth of an organism in water at less than an optimal pH. Bacteria may adapt after an acclimation period to the acidic pH range. Several mechanisms are discussed in Thompson and Wilson (16). Several workers have investigated the effects of acidic conditions on the microflora of aquatic systems (15,17). Weaver (17) compared the species and relative abundance of microflora of two tributaries: an acidic stream (pH 3.0-4.1) which drained an area previously strip mined and the other, a control stream (pH 6.3-6.7) which drained an area relatively unpopulated which contributed no domestic waste. The microflora of the two streams varied noticeably. Table 2 presents an overview of the organisms observed in the two branches. Ferrobacillus ferrooxidans, a bacterium which thrives at pH 2, was consistantly recovered in high numbers from the acid stream but was recovered only once from the control stream. In the control stream high levels of saprophytic bacteria were detected, while considerably lower levels were detected in the acid tributary. The fungi were more numerous and more diversified in the acid stream. Of the 42 different genera identified from samples of the two streams, 21 were seen only in the samples from the acid branch, 4 in only the control stream samples and 17 in both sets of samples. The yeast population of the acid stream was also more diversified. Yeasts were more prevalent in the acid stream during the spring and autumn and in the control stream during the winter and autumn.

From studies investigating the influence of acidic conditions on aquatic microflora in lakes near Sudbury, Thompson and Wilson (15) concluded that factors other than acidity and heavy metal concentrations contributed to the differences or lack of differences seen between populations of bateria, fungi, and yeasts in acidic and neutral lakes. Acid lakes were seen to support similar populations of heterotrophic bacteria and fungi to those supported by neutral lakes in one comparison. In another comparison the neutral lake supported higher numbers of heterotrophic bacteria in the surface waters, but lower numbers in the hypolimnion than the acidic lake. For the same comparison, the fungal population did not vary between lakes in the water, but was found in greater numbers in the sediment of the acid lake.

In a paper by Khulbe (6), reference is made to the works of several scientists who investigated the effects of varying pH levels in surface waters on the species of water molds present. The findings of Suzuki and Hatakeyama corroborate those of Weaver (17). However, studies by four additional researchers showed greater numbers of water molds in waters of near neutral pH values.

Although water does not appear to be an important vector in the transmission of fungal and yeast infections, several of the species of fungi and yeasts observed by Weaver (17) in the two streams have been implicated in cases of human disease. Candida guillermondii has been identified as the causative agent of endocarditis in patients fitted with intravenous catheters, in persons undergoing cardiovascular surgery, and in drug addicts. Gryotococcus neoformans is the only recognized human pathogen of the genus, Cryptococcus. Members of the genera Rhodotorula, Candida, and Torulopsis have been observed in a symbiotic relationship with man. Diseases caused by these yeasts generally occur in persons with compromised immune systems.

The fungi, *Phialophora*, *Cephalosporium*, *Monosporium* and *Cladosporium* have been recovered from infected skin. Species of the order *Mucorales* are considered opportunistic pathogens, in that they usually incite infections only in immunologically defective persons (7).

Not only is microbial growth influenced by the pH of the organism's environment, but so also is microbial virulence. Sauter *et al*. (11) observed maximum penetration rates of three species of salmonellae at pH values of 7.5, 8.5, and 7.0. In the same experiment, the lowest rates of penetration were seen at pH 5.0. The production of enterotoxin by *Bacillus cereus*, an agent of food poisoning, is also governed by pH. When the bacterium is grown under optimum pH conditions of 7.0-7.5, it produces an enterotoxin specific for the cells of the intestine giving rise to the symptoms associated with food poisoning. Spria *et al*. (13) observed very little enterotoxin activity when *B. cereus* was grown in batch culture under conditions more acidic than pH 6.0 or more alkaline than pH 8.5. In experiments designed to investigate the effectiveness of straight lime softening as a means of removing viruses from water, Sproul (14) found loss of viral infectivity in some cases at a pH near 11 (which occurred with excess lime-soda ash softening).

Chlorination is the primary method of disinfection of drinking water supplies in the United States (4). In recent years, the practice has been the topic of many papers and seminars. Several papers have been published detailing the environmental conditions under which various formulations and concentrations of chlorine are most lethal for aquatic microorganisms.

Butterfield *et al*. (3) examined the influence of pH on the survival of coliform and enteric pathogens when exposed to free chlorine. The bacteriocidal properties of free chlorine decreased with increased levels of pH. At pH 7.0 a 100 per cent kill was achieved with a chlorine concentration of 0.03-0.04 ppm in 1-3 minutes. At pH 8.5 a 100 per cent kill required a chlorine concentration of 0.07 ppm and 10 to 20 minutes. The H ion concentration of the test system appeared to influence the relative sensitivity of *Salmonella typhosa*, *E. coli*, and *Pseudomonas aeruginosa* to free chlorine. At pH 6.5, 7.0, and 7.8 *S. typhosa* was more resistant to chlorine concentrations of 0.03 ppm or less, than was *E. coli* which was more resistant than *P. aeruginosa* at pH 7.0. At pH values of 8.5, 9.8, and 10.7 *S. typhosa* was more sensitive to chlorine than was *E. coli* which was more sensitive than P. aeruginosa. (A 100 per cent kill was achieved in 5 minutes at pH

8.5 at a chlorine concentration of 0.06 ppm for S. typhosa, 0.1 for E. coli and 0.15 ppm for P. aeruginosa.)

Although drinking water is deemed potable or not potable on the absence or presence of bacterial indicators potable waters may still contain live viruses. Viruses vary greatly in their sensitivity to chlorine. Reo 1 virus is killed in 2.7 minutes by a free chlorine concentration of 0.5 mg/L at pH 7.0 and a temperature of 2°C. Under the same conditions coxsackie A6 virus can survive contact time exceeding 120 minutes (8).

The particular form of chlorine employed also influences the contact time required to bring about the necessary reduction in viral infectivity. Hypochlorous acid which exists at pH values below 7.5 has been reported to be a more powerful viricide than the hypochlorite ion, chlorine gas, or chloramine (18). However, Scarpino et al. (12) have shown the hypochlorite ion (pH 10) to be seven times more effective against polivirus than hypochlorous acid (pH 6.0). In the same study E. coli was three times more resistant to the hypochlorite ion than was polivirus. Engelbrecht et al. (5) in testing the susceptibility of six enteric viruses to chlorine found a 99 per cent reduction in infectivity of the most resistant virus in 3.4 minutes with a free chlorine concentration of 0.5 mg/l at pH 6.0. Ninety-six minutes contact time was required to produce the same reduction in viruses at pH 10.0.

Various environmental factors also affect the survival of viruses exposed to chlorine (1). It has been shown that viruses associate with particulate matter which offers protection against chlorine. Low temperatures also favour virus survival. It has been suggested that viral progeny surviving an initial exposure to chlorine may become more resistant to chlorine.

Protozoan cysts are resistant to the chlorine residual·concentrations generally maintained in water distribution systems. Cysts are removed from the water supplies by properly functioning flocculation and filtration systems. Bromine has been shown to be a more effective cysticide than either chlorine or iodine. At pH 4.0 a 99.9% cyst mortality occurred in 10 minutes with 1.5 ppm bromine, 2.0 ppm chlorine, and 5.0 ppm iodine. Generally, the cysticide activities of the three halogens decreases with higher pH values (18).

Infectious diseases transmitted by drinking water are primarily those associated with an anal-oral route of transmission. The majority of disease outbreaks have been traced to the use of untreated or inadequately treated water contaminated by human fecal material. Treatment deficiencies are usually the result of improper chlorination, although breakdowns in filtration systems have led to some disease outbreaks. In 1975-1976 most of waterborne disease outbreaks were caused by the consumption of water from semipublic water systems. Far fewer outbreaks were attributed to municipal or individual systems.

As stated earlier, the primary microbial pathogens associated with waterborne infections are bacteria, viruses and protozoa. With the increasing acidity of natural waters the populations of bacteria and protozoa may decrease while those of fungi and yeasts increase. However, it has been shown that bacteria may acclimate to more acidic conditions. Also, lake reclamation studies have shown the relatively fast recovery of bacterial populations, after the pH of the surrounding environment returned to neutral conditions.

Relatively few species of fungi are capable of initiating human disease. These species which do infect humans are limited by their nutritional requirements and the defence mechanisms of the healthy human body. Systemic fungal infections generally result from the inhalation of spores carried by the wind or by traumatic inoculation from contaminated soil or plant materials. Fungal infections are unusual in most hospitals.

Although viruses do not replicate on their own, they are remarkedly resistant to acidic conditions.

An epidemiological study to investigate the influence of more acidic water supplies on the occurrence of waterborne illness and the primary pathogenic species would definitely bridge a gap in the present knowledge. However, given the various conditions associated with waterborne disease, the versatile nature of the organisms known to be waterborne pathogens, and the conditions associated with most fungal infections, it seems unlikely that the present waterborne pathogens would be outranked by fungal pathogens.

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